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FD-30

STUDY OF CARRIER GAS FREEZE-DRYING AT LOW PRESSURES

by

JOHN H. BLAKE

Central Engineering Laboratories
FMC CORPORATION
Santa Clara, California

Contract No. DA 19-129-AMC-369(N)

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U. S. Army Material Command
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FOREWORD

The freeze dehydration of foods is of significant importance to military rations because of the unique combination of good quality with light weight. In the present state of the art, freeze drying is relatively expensive, partly due to long processing times and to low production rates because heat transfer is a limiting factor in the typical commercial process.

Earlier work by FMC Corporation had shown that freeze drying could be accomplished in a flowing stream of inert carrier gas and, moreover, that time reductions over conventional processes were potentially obtainable if appropriate low absolute pressures were used. The objective of the work reported here was to carry out an extensive exploration of the technical feasibility of this process when using a condensible carrier gas.

The work covered in this report was performed by FMC Corporation, Central Engineering Laboratories, under Contract No. DA19-129-AMC-369(N), during the period from 1 July 1964 through 30 June 1965. The investigator was Dr. John H. Blake and his collaborators were E. Gyuline, J. Lennon, J. Roe, A. Teller, and M. G. Miller.

The U. S. Army Natick Laboratories Project Officer was Dr. Roger M. Stinchfield and the Alternate Project Officer was Mr. John Swift, both of the Food Division. The Contracting Officer was Mr. John Lynch of the Purchasing and Contracting Office.

FERDINAND P. MEHRLICH, Ph.D.
Director
Food Division

APPROVED:

DALE H. SIELING, Ph.D.
Scientific Director

W. W. VAUGHAN
Brigadier General, USA
Commanding

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ABSTRACT

This report covers an investigation of a process to freeze-dry at increased rates by using condensible carrier vapors to transfer heat to frozen food particles (LPCS process). About 20 common foods were successfully dried. Optimum pressures are 3 to 15 mm Hg @ 130-150°F. A mixture of heptane isomers purified with fuming sulfuric acid appears to be the best carrier fluid for large-scale work, but formation of a solid hydrate in the condenser is a complication. Drying times ranged from 2 to 6 hours, and can be affected greatly by processing conditions.

SUMMARY

Earlier work by FMC Corporation had shown that the Low Pressure Carrier Sublimation Process(LPCS), in which a condensible vapor circulates through a bed of particulate food at a total pressure of 5 to 15 mm Hg, can transfer heat to the food particles and sweep away water vapor so that the food rapidly freeze-dries. Beds of food from 3 inches to 12 inches deep had been freeze-dried in times between 2 and 4 hours.

The objectives of this work were to verify these preliminary results; to investigate the variables, such as food type and particle size, temperature, pressure, etc.; to prepare samples sufficiently large for stability and quality studies; to determine the desirable properties for a carrier fluid; and to study other factors affecting the process.

The results of small-scale work showed that foods low in sugar and sufficiently permeable, such as diced meats, shrimp, and cooked vegetables, freeze-dry very well under the conditions of LPCS. Sliced strawberries also freeze-dried satisfactorily at about 3 mm Hg, but at higher pressures (6 to 8 mm Hg), they thawed and shrank.

Increasing the pressure from 3 to 50 mm Hg caused the drying rate of cooked beef to increase at first, and then to level off, at about 15 mm Hg. There may have been a maximum rate at about 15 mm Hg, but the measurements were not sufficiently precise to verify this.

Heptane was used as a carrier fluid for most of the work, but FC-75 (a cyclic fluoroether $C_8F_{16}O$) and hexane were evaluated and appeared to be satisfactory.

Any aromatic impurities in the heptane were preferentially adsorbed by the dried food and imparted an undesirable taste, but it was found that technical grade heptane, which is a mixture of isomers and has a considerable content of aromatic impurities, can be adequately cleaned with fuming sulfuric acid, to serve as a satisfactory and inexpensive carrier fluid.

A pilot-scale apparatus was constructed and this ran very well, except that the unexpected formation of a solid hydrate of heptane and water in the condenser, complicated the operation and limited the duration of the runs. A modification in design could undoubtedly handle this problem if another apparatus were built. Despite this difficulty, 1/2-to 4-pound (dried weight) samples of 9 foods were freeze-dried.

An economic analysis of the LPCS process, performed at the contractor's own expense, showed that on a large scale, it could freeze-dry the foods for which it is suitable at approximately 15% to 20% less cost than with conventional vacuum freeze-drying.

I. INTRODUCTION

A. Background

Previous work by FMC Corporation and by Harper (1, 2) demonstrated that the time to freeze dry a bed of particulate food can be decreased considerably from that usually required by vacuum freeze drying if an inert carrier gas is made to flow through the bed. Under proper conditions the stream of carrier gas will transfer the heat required for sublimation to the frozen food particles and will sweep water vapor away and so maintain a sufficiently low partial pressure of water adjacent to the food. To freeze dry in this manner at atmospheric pressure, the temperature of the carrier gas can only be a very few degrees above the freezing point of the food if melting is not to occur. By reducing the pressure of the carrier gas, however, water vapor will diffuse through the dried part of the food pieces more rapidly and therefore gas at higher temperature can contact the food without melting it. In this way a given amount of carrier gas can transfer more heat to the food particles which therefore enables drying to take place much more rapidly at these lower pressures. As pressure is lowered from atmospheric down to the range of 5 to 20 mm Hg, the thermal conductivity of the carrier is virtually unaffected; but since the diffusivity of water vapor through the inert carrier becomes much greater, high rates of freeze drying are possible in this range of pressures. At pressures lower than these, the thermal conductivity of the carrier fluid and thus of the dried shell of food surrounding the ice core decreases. This is the principle of the LPCS process.

The LPCS process thus involves the circulation, dewatering, and reheating of very large volumes of gas at these low pressures. To cope with this problem, Barth and co-workers (3) proposed the use of a condensible carrier fluid so that the large volumes of gas or vapor could be generated by vaporizing a liquid above the bed and condensing the vapor after it had passed through the bed and conveyed water vapor from it.

Since beds of diced meats loaded to more than 20 pounds per square foot had been freeze dried in less than 4 hours by use of the condensible carrier, the scheme showed promise for freeze drying certain foods at considerably less cost than is presently the case. For this reason, and because freeze dried foods are so promising as rations for troops to carry in the field, a proposal to pursue this work further was submitted to U. S. Army Natick Laboratories.

This is the final report describing the work carried out under the contract resulting from the above proposal.

B. Objectives

The general objective of this contract was to investigate the freeze drying of foods by use of a condensible carrier gas at low pressures within the range of 1 mm to 200 mm Hg.

The program delineated by the contract entailed small scale trials with 15 or 20 common foods to assess the suitability of the LPCS method; an

investigation of process and operating variables to determine their effect on the rate of freeze drying and on the quality of the resulting product; preparation of 10-pound samples of dried foods by both the LPCS and conventional vacuum freeze drying processes for submission to U. S. Army Natick Laboratories to use in their evaluation and storage studies; a study of possible carrier fluids; and other pertinent factors which might arise from the investigation, such as residues of carrier fluid in the dried food.

C. Work Accomplished

The objectives of the small scale work are believed to be fairly well accomplished, although a comprehensive investigation of the many parameters considered was not possible within the scope of the contract.

A pilot scale drying unit was made by modifying an existing apparatus and it was designed to use heptane as a carrier since this fluid is cheap and the FDA has already established tolerances for it. The use of heptane, while an advance over the previous work, gave rise to unexpected complications with the pilot scale apparatus which prevented the drying of as much food as had been desired without exceeding the available funds. The principal difficulty involved the formation of curdy suspended solids in the condensed heptane. As a drying run progressed, these solids built up in the system to the extent that they interfered with the circulation of carrier. Thus the amount of food that could be dried in a given batch and the rate of circulation of carrier fluid were less than had been anticipated; and the production of samples totaling several pounds was quite difficult. However, with the experience gained in this work, it appears that suitable equipment can be designed to cope with these solids (which seem to be a hydrocarbon hydrate).

A second difficulty with the larger scale apparatus was that sufficiently large quantities of adequately pure heptane were not readily available. A procedure was developed to purify the heptane, so that it should be possible to prepare sufficient fluid for any large scale unit.

D. Principal Conclusions

1. The LPCS process can rapidly and satisfactorily freeze dry particulate foods whose melting temperatures are not too low and whose pore structure is sufficiently permeable. This includes cooked, diced beef and chicken, cooked shrimp, fish, leafy vegetables, and diced strawberries. Peaches, apples, carrots, peas, and whole kernel corn melted in the drier (although the dried materials did rehydrate quite readily), so the process is somewhat limited in the foods which it can freeze dry.

2. The drying rate increases with pressure, and it may possibly go through a shallow maximum at 10 to 15 mm Hg for diced cooked beef.

3. The maximum pressure is limited by either the dew point of the carrier fluid or by melting of the food.

4. Aromatic compounds must be thoroughly removed from the carrier fluid, since the dried food seems to adsorb them preferentially, and they impart a strong unpleasant taste to the food.

E. Preliminary Design and Economic Study

Although a design and economic study was not within the program set forth by the contract, FMC Corporation, at its own expense, developed a preliminary concept for a plant to freeze dry 2,000 pounds of food per hour by this process in order to assess the potential economics of LPCS. The results of this work are briefly presented in this report (Appendix V).

The cost of freeze drying by LPCS is estimated to be 4.7¢ per pound of water evaporated. On a comparable basis the estimate for conventional vacuum freeze drying is 5.4¢ per pound. A large and continuous production of suitable food (e. g. diced chicken) would be necessary to realize this cost advantage, and at the present other factors, including insufficient demand for such dehydrated foods, argue against commercial use of the process.

F. Format of the Report

The principal topics covered by this report are treated in six separate and fairly self-contained sections of which this Introduction is the first. The detailed data and calculations are presented in the Appendix.

II. PRELIMINARY LPCS DRYING TESTS ON 20 COMMON FOODS

A. Small Scale Drying Apparatus

1. Figure II-1 shows a flow sheet of the apparatus used for this part of the work. Figures II-2 and II-3 are photographs of the whole apparatus and of the sample holder. Referring to Figure II-1, the carrier liquid, which was normal heptane in all of this work, flows from a storage container, through a rotameter, and then to a needle valve where the flow is regulated manually. The liquid passes into the vaporizer which consists of several feet of 3/8" copper tubing immersed in a constant temperature water bath, kept at 150° for these runs. Carrier vapor at low pressure then enters the drying chamber, which is a 12" long section of Pyrex pipe 4" in diameter, sealed at the ends with 3/8" aluminum plate. The vapor passes through the sample in the sample holder inside the drying chamber, then from the bottom of the drying chamber it goes to the condenser which is in turn connected to the vacuum pump.

   The top of the drying chamber and the vapor line into it are maintained at 150°F by infrared lamps. A transparent plastic water jacket surrounds the walls of the drying chamber with hot water of the desired temperature circulating through it.

   Pressure in the drying chamber is regulated manually by throttling the vapor at the chamber's outlet. It is thus necessary to keep the temperature of the condensing vessel below -10°F or -20°F so the vapor pressure of the condensed carrier will be considerably less than the chamber pressure. The condenser is a stainless steel oxygen bottle about 12" in diameter by 18" high and it is immersed in propylene glycol and dry ice.

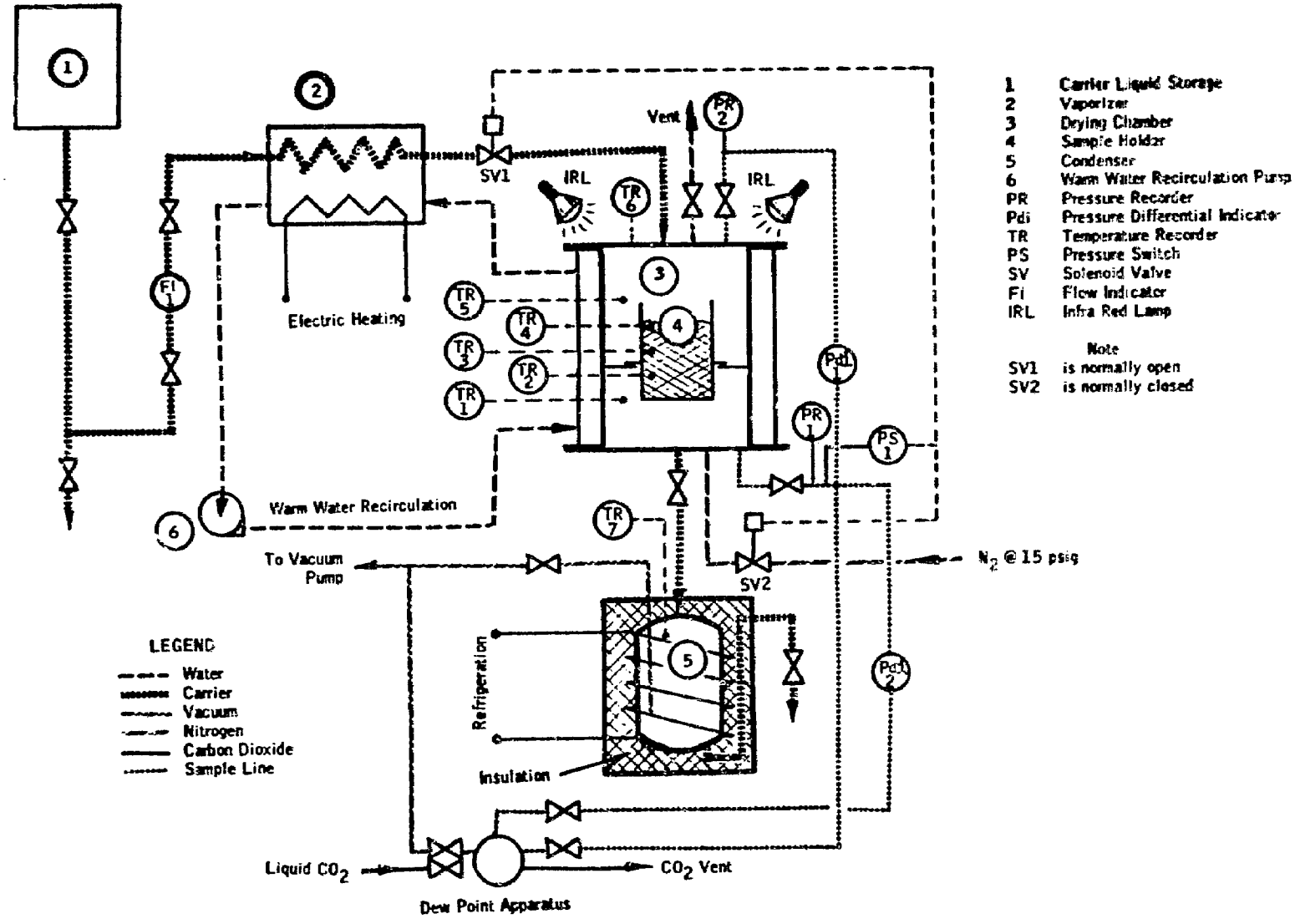


FIGURE II-1 SCHEMATIC-SMALL SCALE APPARATUS FOR FREEZE DRYING WITH A CARRIER GAS

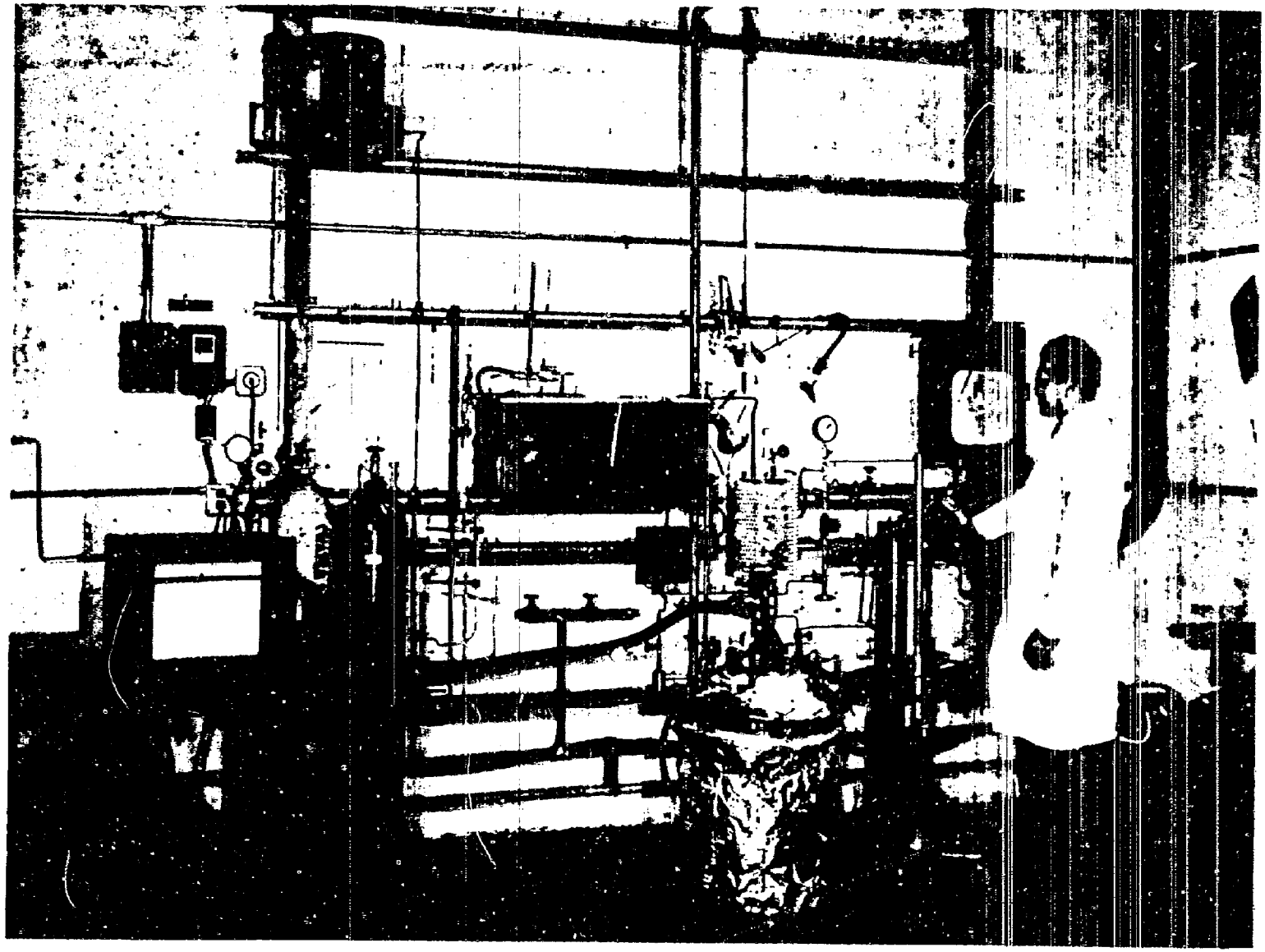


FIGURE II-2 SMALL SCALE LPCS APPARATUS

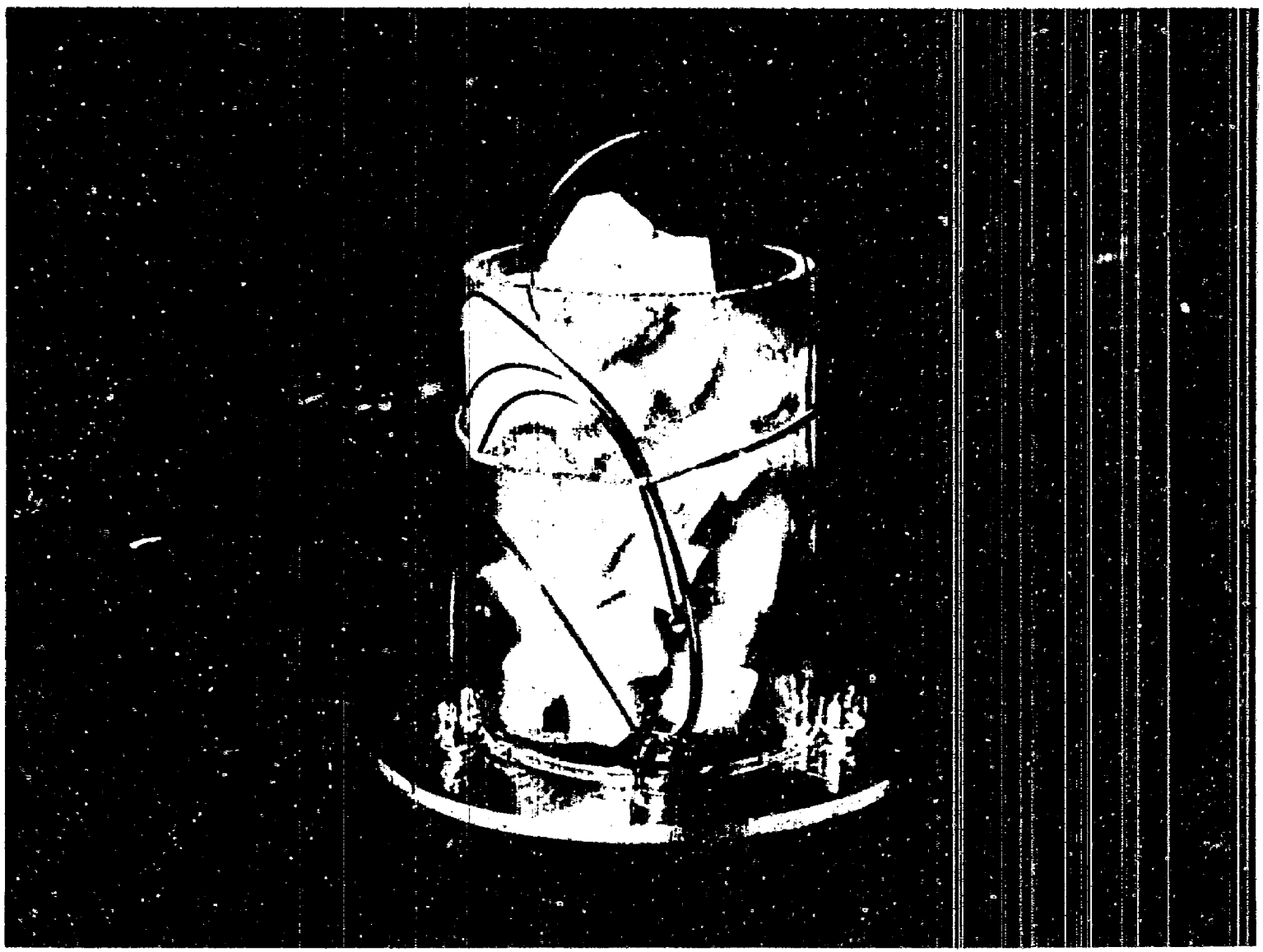


FIGURE II-3 FOOD BED, SMALL SCALE LPCS APPARATUS

The sample holder is a transparent plastic cylinder 2" in diameter and 3" deep equipped with five double conductor jacks so that five thermocouples can be connected between the holder and a temperature recorder. Ordinarily a 36 gauge copper-constantan thermocouple is placed above the bed, 3 are in the bed at the top, middle, and bottom, and one thermocouple is below the bed. (See Figure II-3.)

There is some uncertainty about the validity of the temperature measurements. The couples above and particularly below the bed attempt to measure temperature of the gas flowing past them but they also receive radiation from the warm walls of the chamber. Fine wire and a reflective junction of shiny solder were used to minimize radiation, therefore the indicated temperatures of the gas entering and leaving the bed should be reasonably accurate. Thermocouple junctions inside the bed are located at the center of food particles in a hole made with a small awl and sealed by a drop of water which is then quickly frozen. With small food particles, such as kernels of corn and split peas, the particle temperatures recorded are undoubtedly too high, since appreciable heat can conduct from the warm gas flowing past the particle through the metal wire to the thermocouple junction inside the particle. However, these particle temperatures as measured are useful because they represent an upper limit, with the actual temperature being lower than that indicated, and their variation with time provides a guide to the course of the run.

To avoid developing an explosive mixture of gases in the system, a pressure switch is connected to the bottom of the drying chamber. If the absolute pressure in the chamber rises above about 50 mm Hg (or if the power fails) the switch opens and stops the flow of heptane by closing the solenoid valve in the carrier supply line. Opening the pressure switch also opens the solenoid valve in the nitrogen supply and so purges the system.

2. The procedure for making a run is as follows:

   a. The tared sample holder is loaded with frozen sample, quickly weighed, and taken into the cold room. Here the thermocouples are arranged and the sample is stored in a sealed container while the drying apparatus is brought up to temperature and charged with a weighed amount of carrier liquid.

   b. The sample holder is placed in the drying chamber, the thermocouples are connected, the top is placed on the chamber, and the apparatus is quickly evacuated. When the pressure is less than one millimeter, the flow of carrier is adjusted to its proper rate with the valve downstream from the rotameter. At the same time the pressure in the apparatus is regulated manually by the valve at the outlet of the drying chamber. The flow of carrier and the pressure in the chamber are carefully controlled during the course of a run.

   c. When the temperatures throughout the sample have risen to that of the vapor entering the chamber, the flow is stopped, the chamber is briefly evacuated, and then the vacuum is broken with nitrogen.

d. The sample is quickly transferred to a tared sample jar whose cover is put loosely in place and the jar is then evacuated in a desiccator. The vacuum is broken with nitrogen, the desiccator is re-evacuated and this cycle is repeated two or three times to purge oxygen from the sample container. Then the desiccator is opened, the top is screwed tightly on the sample jar, and it is weighed.

B. Examination of the Dried Foods

1. The appearance of the dried sample is carefully noted when it is removed from the drying chamber. If the particles are shrunken and glazed, they have probably thawed during drying. In several cases a run was terminated before drying was complete and the food was quickly removed and examined to see if it had thawed. When the centers were found to be frozen, freeze drying was conclusively demonstrated.

2. Moisture content of the dried sample was determined by observing the loss of weight of an aliquot after sixteen hours at 150°F in a vacuum oven at about 50 mm Hg total pressure. Moisture in samples of undried foods was determined in the same way.

3. Retention of water by the dried sample was determined by weighing dry, immersing in water at 160°F for either five or fifteen minutes, removing the adhering moisture by blotting lightly with a paper towel, and reweighing the wet sample. Results are reported as weight of water absorbed per unit weight of dried sample.

4. The samples hydrated for five and for fifteen minutes were tasted by two or three people who commented on flavor, odor, and consistency in qualitative terms.

   In several instances the taste test was obscured by the fact that the drying and rehydration did not cook a sample sufficiently to do away with an unfamiliar raw flavor. Raw fish, mushrooms, and broccoli were three such cases, and this fact should be considered as Table II-1 is studied.

C. Source of Food Samples

Since the preliminary work was designed to explore the behavior of fifteen or twenty common foods in this process, only readily available materials were used. Samples were either frozen foods purchased from a local retail market or they were fresh foods cut to the desired size and frozen here. Table II-1 notes the preparation very briefly. The vegetables were all obtained in the frozen state, while the fruits, meat, and fish were purchased fresh, cut and frozen quickly in this laboratory.

D. Presentation of Data

Table II-1 summarizes the results from the trials of twenty foods to determine their behavior in this process. For most of the runs a nominal drying

TABLE II-1

VARIOUS FOODS DRIED IN HEPTANE VAPOR

Run No.	Moisture, Wt% before	Moisture, Wt% after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft²	Flow #/ft²-min.	Retention #H₂O / # dry food	Time Stored Days	Results
1. Vegetables										
a. Corn - whole kernel, IQF										
6		5.8	210	150	6.0	8.2	2.27	.92		Some shrinkage*, dry. Natural flavor & color when rehydrated.
17	-	-	30	150	6.0	3.7	2.27			Run stopped, all kernels thawed and none were dry.
Corn, above sample, steamed approximately 50 min., drained, refrozen										
48		5.3	140	150	6.0	2.3	2.20	1.26	3	Some shrinkage, when dry. Good flavor and color, rehydrated.
Corn - whole kernel, IQF - variation of temperature and pressure										
60	72.25	4.3	210	150	6	8.47	2.21 1.24	0.82	4	Shrunken. Dry, tough texture. Good flavor.
61		2.0	240	100	4	2.64	0.69	0.94	3	Starchy consistency. Tough texture. Fair to good flavor. Some shrinkage.
62		2.6	95	130	4	2.38	0.79	1.91	3	Fair to good texture. Very good flavor.
65		-	205	130	6	7.75	0.97 1.04	(Sample for sulfite analyses)		Some shrinkage. Color unchanged.
69		-	210	130	6	8.30	1.04	"		Shrunken, some melting, color unchanged.
70		-	225	130		6.80	1.04	"		Shrunken, some melting, color unchanged.

* Shrinkage observed on dried sample; taste, odor and texture observed after 15 min. rehydration at 180°.

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft²	Flow #/ft²-min.	Retention #H_2O # dry food	Time Stored Days	Results
		Whole kernels								
96*	71.6			150	6	-	-	-		Badly shrunken. Dry starchy taste.
		Kernels cut in half								
97*	71.4			150			-	-		Much less shrinkage. Better taste and more succulent texture than No.96
	Corn - whole kernel, cooked - boiled 5 min; drained, refrozen									
50		5.5	230	150	6	3.09	2.21	1.15	15	Color unchanged. Some shrinkage. Fair taste. Tough, sticky texture.
51		-	39	150	6	2.37	-	-	-	Opened for observation. Melted insid
	b. Carrots - diced, fresh frozen									
5	87.4	3.3	290	150	6.0	6.5	1.10	.95		Some shrinkage, dry. Natural flavor and color, rehydrated.
36	87.4	3.4	255	150	3.0	7.0	1.10	4.52	4	Some shrinkage and cracked, when dry. Soggy, fair flavor of raw carrot rehydrated.
	c. Broccoli - chopped, fresh frozen, approximately 1/8" pieces									
32	91.1	2.7	185	150	6.0	4.0	1.10	5.89	11	Bright green color. Stems shrunken. Tough, flavor of raw broccoli.
	d. Spinach - chopped, fresh frozen block, broken into approximately 3/8" pieces.									
33	91.8	2.2	280	150	6.0	4.6	1.10	3.79		Drying not complete - sample from top of bed. Bright green color. Soggy, flavor of raw spinach.
63	91.75	4.9	180	150	6	3.94	1.24	4.92	2	Good texture. Good flavor. Color unchanged. No shrinkage. No melting

* Approx. 7 gram samples for weight-time data.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft²	Flow #/ft²-min.	Retention #H₂O # dry food	Time Stored Days	Results
64		-	65	150	6	2.32	1.24	-	-	Stopped for observation. Not dry, (ice inside) color unchanged.
	e. Beans, green, French cut. Fresh frozen									
34		4.2	210	150	6.0	3.9	1.10	5.47	5	Some shrinkage. Crisp, flavor of raw beans.
	f. Beans, green, Italian. Cut in approximately 3/4" lengths									
35		8.9	270	150	6.0	5.5	1.10	3.52	5	Quite shrunken. Light green with dark waxy areas. Crisp, fair flavor of raw beans.
	g. Potato, fresh frozen, chopped for hash browning									
37	88.31	3.1	140	150	6.0	5.6	2.20	4.02	3	White color. No shrinkage apparent. Flavor of raw potato.
	h. Mushroom, fresh frozen. Approximately 1/4" cubes									
42	90.0	0.5	110	150	6.0	2.0	2.20	3.20	9	Color unchanged. Slight shrinkage. Soggy texture. Bitter flavor of raw mushrooms.
	i. Peas - fresh frozen. Each pea cut in half									
43		1.8	125	150	6.0	4.2	2.20	2.68	6	Inside slightly shrunken, mostly light green with waxy, shrunken dark green spots in places under skin. Texture of cooked peas. Taste good.
	Peas - whole, same lot as above sample, steamed 5 min. Skin of each pea punched									
44		4.0	120	150	6.0	4.0	2.20	2.41	5	Slight shrinkage. Consistency and flavor of well-cooked peas.
	Peas, IQF (Each pea cut in half)									
49	74.9		70	150	6	3.20	2.21	-	-	Color lighter. Some shrinkage on inside.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	Moisture, Wt% after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft²	Flow #/ft²-min.	Retention #H₂O # dry food	Time Stored Days	Results
			Peas, scarified while frozen							
93*				150	6				66	Color unchanged, good texture and taste. Considerable melting inside.
			Peas, cut in half while frozen							
94*				150	6				65	Color unchanged, softer texture, good taste. Less melting.
			Peas, crushed while frozen							
95*				150	6				64	Color unchanged, softer texture, good taste. Hardly any melting.
2. Fruits										
			a. Strawberry, sliced, IQF							
			Sliced 3/8" thick							
98	90.87	2.83	440	130	3.5	7.27	.63	-	6	Color unchanged. Some shrinkage. No melting evident.
			Diced to 3/8" x 3/8" x 3/8" pieces							
99		4.19	340	130	3.5	7.90	.63	-	5	Color unchanged. Some shrinkage. No melting evident. Texture of the pieces are uniform throughout.
			Cylinders 3/8" x 3/8" diameter							
100*				130	3.5				57	Musty, flat taste.
			b. Apple - fresh, cut into approximately 1/4" cubes, frozen							
39	84.2	.5	255	150	3.5	6.0	1.65	1.40	12	Shrunken. Glazed on surface. Soggy texture. Pleasing taste and odor.

* Approx. 7 gram samples for weight - time data

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft^2	Flow #/ft^2-min.	Retention #H_2O # dry food	Time Stored Days	Results
41	84.2	2.0	160	150	3.5	5.8	1.65	1.36	10	Shrunken. Glazed on surface. Soggy texture. Pleasing taste and odor.
	c. Pear, fresh, cut into approximately 1/4" cubes, frozen									
40	86.1	4.0	155	150	3.5	-	1.65	1.39	13	Shrunken. Glazed surface. Limp texture. Taste good. Hint of hydrocarbon flavor.
	d. Peaches, fresh, cut into 3/8" cubes and frozen									
38	88.3	3.5	200	150	3.5	5.5	1.65	1.55		Natural color. Shrunken. Mushy texture good flavor.
	Peaches, Rio Osa Gem, treated with sulfite and ascorbic acid. IQF									
	Cut to cubes 1/4" x 1/4" x 1/4"									
53	88.4	6.4	145	150	4	3.23	1.73	1.97	11	Soggy. Shrunken. Good flavor.
54		5.3	249	130	4	3.27	1.76	1.72	10	Color unchanged. Some shrinkage and melting on the surface. Soggy texture. Good flavor.
55		4.6	235	130	4	2.31	1.76	2.77	9	Color unchanged. Some shrinkage and melting on the surface. Soggy texture. Good flavor.
56			165	130	6 to 3	2.50	2.56 1.87 1.21			Color unchanged. Very shrunken. Some melted.
58			210	100	0.5 3 to 5	2.80	1.8 to 1.5	-	-	Not dry. First hour no heptane, only radiation, at 0.5 mm Hg.
59		6.4	240	100	0.7 2.5	3.11	1.49	1.60	7	Color unchanged. Some melting and shrinkage. Soggy texture. First hour, no heptane, 0.7 mm Hg.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft^2	Flow #/ft^2-min.	Retention #H_2O # dry food	Time Stored Days	Results
		Cut to triangles 1/4" thick with sides 1" x 1" x 1-14" to 1-1/2"								
66	88.4	4.0	270	150	3.5	6.32	.48 to .76	2.53	7	Color changed slightly. Shrunken and some melting. Good flavor. Chewy, soggy texture.
67		18.0	240	100	0.5 3.5	1.54	0.48	2.25	6	Color changed. Shrunken and some melti Not dry. Brown, soggy. (trace of hepta Good to fair taste.
		Cut to triangles as above, sample was thawed for one hour and re-frozen.								
79	88.4	13.5		100	3.5	6.07	0.48	1.17	4	Color unchanged. Shrunken and some melting. Good flavor.
		Cut to triangles as above, Samples vacuum freeze-dried								
68	88.4	1.9	16 hrs.	100	0.05	-	-	2.7	6	Shrunken and melted, soggy texture. Good flavor and odor.
76		I. Thawed at 30° for 3 hrs; refrozen								
	88.4	1.5	16 hrs.	100	0.05	-	-	2.5	7	Brown. Somewhat shrunken. Fair texture and flavor.
		II. Thawed at 30° for 1 hr; refrozen								
		1.6	16 hrs.	100	0.05	-	-	1.7	7	Color good. Some shrinkage. Fair textu and flavor.
		III. Not thawed								
		.9	16 hrs.	100	0.05	-	-	1.7	7	More shrinkage than I and II. Fair te and flavor.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft^2	Flow #/ft^2-min.	Retention #H_2O # dry food	Time Stored Days	Results
3. Meats										
a. Beef, raw, lean. Approximately 1/2" cubes										
45	73.7	1.2	220	150	6.0	4.4	2.20	1.33	4	Color slightly brown, crystaline structure on inside. Little shrinkage. Tough. Good flavor and odor.
46	73.7	-	115	150	6.0	4.3	2.20	-	-	Not dry. Thawed on inside. Freeze dried on outer 1-2 mm.
Raw Beef - cross rib quick frozen on open tray										
Diced at 1/4"										
92	71.6	1.26	155	150	6	6.5	1.24		60	Color same throughout. No melting evident. Good texture when rehydrated. Beef flavor, but foreign taste also.
Diced (most pieces 1" x 1/4" x 1/4")										
75		.85	250	150	6	6.53	1.24	1.33	7	Color of sample changed slightly to brown outside. Some melting inside on every piece.
Ground through 3/8" holes										
74		.62	200	150	6	6.74	1.24	1.49	7	Larger pieces darker and hollow inside, as if melted. Smaller pieces uniform throughout.
Ground through 1/2" holes (pieces cut 1/2" x 1/4" x 1/4")										
78		.68	150	150	6	6.55	1.24	1.17	5	Some shrinkage. Smaller pieces dried all right. Inside larger pieces there was some melting.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft^2	Flow #/ft^2-min.	Retention #H_2O # dry food	Time Stored Days	Results
				Ground through 1/2" holes (pieces approx. 1-14" x 3/4" x 1/6")						
77		.77	215	150	6	6.33	1.24	1.25	6	Color changed to brown outside. Smaller pieces were uniform throughout, as if no melting. Larger pieces hollow inside.
	Beef - Swiss steak, raw. 1/4" tc 3/8" cubes									
28	75.1	1.8	230	150	6.0	4.5	1.10	1.25	4	Not shrunk. Brown color. Chewy. Good Flavor.
Control (Vacuum freeze dried)										
	75.1	0.3	16 hrs.	150	0.3 (approx.)			1.31		Good taste and odor.
b.	Beef - Swiss steak, cooked, cubed 1/4" to 3/8"									
27	61.8	1.7	185	150	6.0	3.6	1.10	.75	4	Appearance unchanged. Good flavor. Possible foreign odor.
29	61.8	-	90	150	6.0	3.6	1.10	-	-	Not dry. Top - small ice core. Bottom - larger ice core. No melting.
Control (Vacuum freeze dried) Same sample as above.										
	61.8	0.3	16 hrs.	150	0.3 (approx.)			1.16		Taste and odor good.
	Cooked Beef (cubes 1/4" x 1/4" x 1/4") dried with water vapor as carrier gas									
52	73.69	6.5	195	150	2.5	3.21	0.48	1.01	14	Sample was not dry. No melting apparent. Some shrinkage. Good texture. Very good flavor and consistency, with dried piece

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft2	Flow #/ft2-min.	Retention #H2O # dry food	Time Stored Days	Results
c. Chicken, cooked, white meat. Diced approximately 1/4" cubes, frozen										
21	67.5	-	180	150	6.0	3.4	1.65	1.63	6	No apparent shrinkage. Tender. Odor and flavor good. Possible taste of heptane.
22	67.5	0.1	180	150	6.0	3.5	1.65	1.58	5	Same as above.
Control										
	67.5	0.7	16 hrs.	150	0.3 (approx.)			1.77		Taste and odor good.
d. Chicken, baked at 350° 1-1/2 hrs, dark meat, diced approximately 1/4" cubes, frozen										
23	66.6	1.8	140	150	6.0	3.3	1.65	1.41	6	No apparent shrinkage. Texture, odor, and flavor good.
24	66.6	-	60	150	6.0	3.7	1.65	-	-	Not dry. Top of bed, good ice core, but thawed near thermocouple. Bottom, larger ice core. Fat melted in dried meat.
25	66.6	2.2	185	150	6.0	3.9	1.10	1.47	4	Not shrunken. Dark spots of fat on dried pieces. Good flavor, odor and texture.
26	66.6	-	75	150	6.0	3.6	1.10	-	-	Not dry. Ice cores well frozen at top and bottom of bed.
Control										
	66.6	.5	16 hrs.	150	0.3 (approx.)			1.22		Very good taste and odor.
4. Fish										
a. Shrimp, raw, cleaned, cut into approximately 3/8" x 3/8" in diameter sections. Frozen										
31		0.5	310	150	6.0	6.5	1.10	1.60		Darker red. Very slight shrinking. Taste good.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp °F	Pres. mm Hg	Loading #/ft²	Flow #/ft²-min.	Retention #H₂0 # dry food	Time Stored Days	Results
	b. Shrimp, cooked, cut into approximately 3/8" sections. Frozen									
30		0.7	300	150	6.0	7.0	1.10	2.35		Color unchanged. No shrinking. Very good taste.
	c. Halibut, raw, cut into approximately 1/2" cubes. Frozen									
16	77.9	-	50	150	6.0	3.8	2.20	-	-	Not dry. Wall frozen ice cores. No thawing evident.
18	77.9	0.8	185	150	6.0	2.9	1.10	1.94	9	No shrinkage evident. Stringy. Taste fair.
19	77.9	1.5	-	150	6.0	3.2	1.65	1.81	7	No shrinkage. Fair taste.
20	77.9	-	160	150	9.0	3.9	1.65	1.77	7	No shrinkage. Fair taste.
	d. Rock Cod, fresh filet cut into approximately 1/2" cubes. Frozen									
47	76.1	0.9	200	150	6.0	3.7	2.20	1.52	3	Outside, no shrinkage evident. Inside had different structure, as if melting may have occurred.
	e. Fish - Ling Cod									
	Large Dices (most of pieces were parallelepipeds 1" x 1" x 1/2" while some of them were parallelepipeds 1/2" x 1/2" x 1/2")									
71	76.9	1.3	200	150	6	6.78	1.24	2.88	3	No shrinkage or very little. Dry flaky texture. Fair taste when rehydrated and cooked. Natural Cod color.
	Small Dices (most of the pieces were parallelepipeds 1/4" x 1/4" x 1/4"; some were parallelepipeds 1/4" x 1/2" x 1/2")									
72		0.9	185	150	6	6.80	1.24	1.91	8	Color unchanged. No melting. No shrinkage or very little. Good flavor and texture.

Table II-1 (Cont'd)

Run No.	Moisture, Wt% before	after	Time Min.	Temp. °F	Pres. mm Hg	Loading #/ft^2	Flow #/ft^2-min.	Retention #H_2O # dry food	Time Stored Days	Results
Intermediate Dices (most of the pieces were parallelepipeds 3/4" x 1/4" x 3/4"; some were parallelepipeds 1/2" x 1/2" x 1/4")										
73		1.3	185	150	6	6.98	1.24	1.86	8	Color unchanged. No melting. No shrinkage or very little. Good flavor and texture.

Table II-1 (Cont'd)

temperature of 150°F was selected, and the total pressure in the drying chamber was 6 mm Hg in most cases. The pressure drop through a sample due to the flow of vapor was quite small and never amounted to more than 1/2 mm Hg. Depth of sample bed varied from 1-1/2" to 3". Table II-1 shows for each sample a very brief description of its preparation, the run number, its moisture content before and after drying, the total time in the drier, nominal drying temperature, and chamber pressure. The sample loading in terms of pounds per square foot of bed cross section, the flow of carrier vapor in pounds per square foot of bed per minute, the moisture retention of the sample, and the approximate time that the sample was stored between drying and testing are also given. Shrinkage and appearance of the dried sample are described and the flavor, texture, and odor of the rehydrated sample is noted.

There was never any significant difference between samples rehydrated for five minutes and those rehydrated for fifteen minutes, even though several of these materials thawed during drying, and shrank considerably. The shrunken samples recovered their original shape to a considerable extent on being rehydrated. Figure II-4 shows some of the dried foods.

E. Behavior of Various Foods

1. Vegetables

a. Whole kernel corn, either raw or cooked, shrank somewhat on drying and undoubtedly thawed before it was dry. However, the dry material seemed to hydrate readily and it gave a product which had the taste and consistency of ordinary frozen or canned corn. The skin on a corn kernel must impede diffusion of water vapor to the outside enough so that temperatures above its freezing point developed. Even at 100°F and 4 mm Hg kernels shrank somewhat and apparently thawed. Only when the frozen kernels were cut in half before drying did true freeze drying seem to take place. These split kernels dried with much less shrinkage and the product had a better taste and texture than any of the other samples of corn.

b. The carrots also shrank on freeze drying and they too hydrated readily and resembled normal cooked carrots.

c. Chopped broccoli retained its green color, but the stems were shrunken and cracked. Probably the flowers and leaves freeze dried but the stems did not.

d. The chopped spinach freeze dried very well at 150° and 6 mm Hg.

e. French cut green beans shrank on drying, but appeared to rehydrate satisfactorily.

f. Cut green Italian beans were quite shrunken, with dark waxy areas which did not appear to rehydrate well.

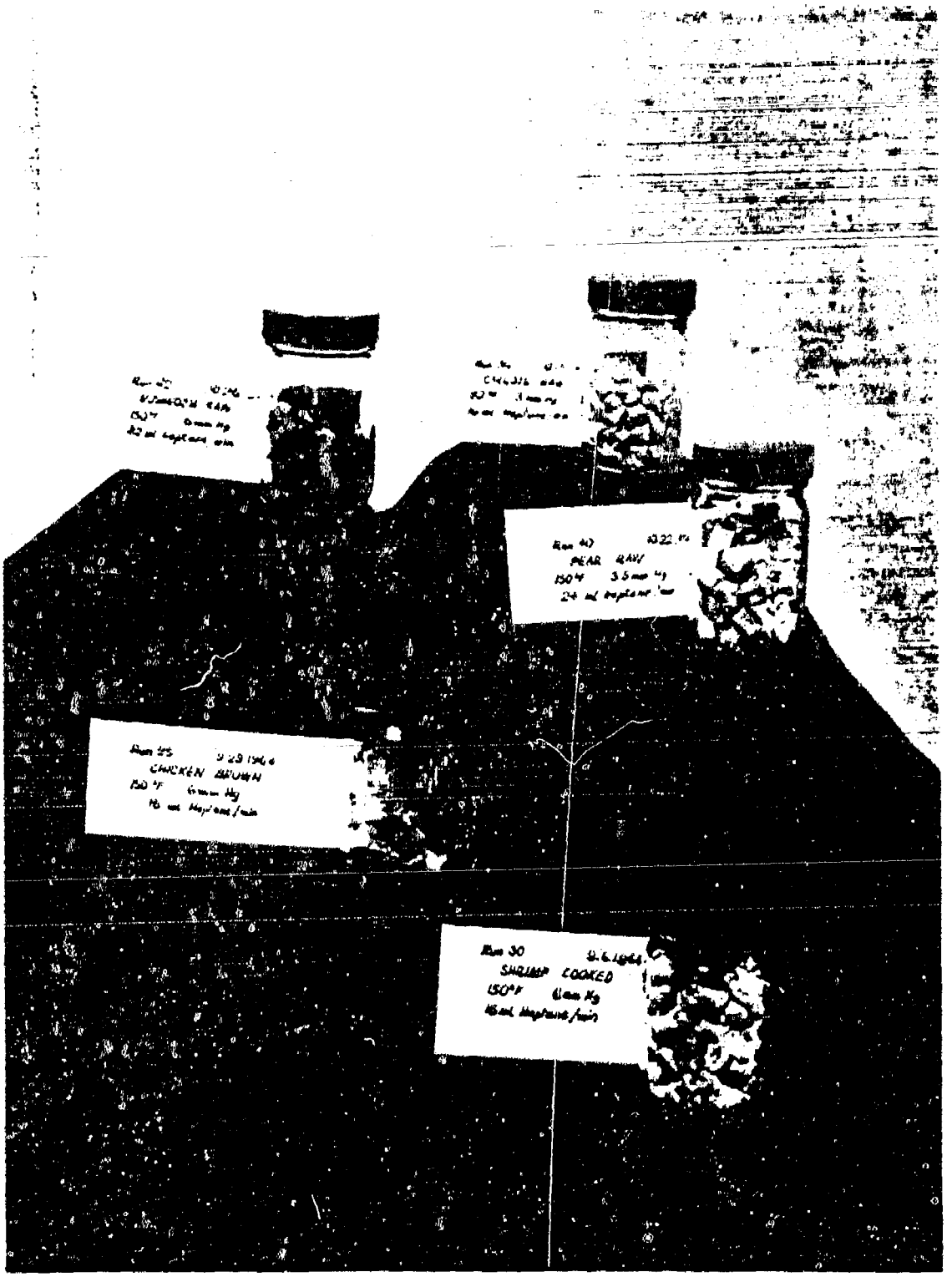


FIGURE II-4 PRODUCTS DRIED IN SMALL SCALE APPARATUS

g. The potatoes dried without shrinking and rehydrated very well.

h. Fresh mushrooms were cut and frozen. The thick part of the samples shrank to some extent, but the product appeared to rehydrate readily.

i. Peas were split in the frozen state before drying. On drying the inside appeared to have shrunk away from the skin a little bit and was for the most part light colored and quite porous. However, many half peas had a dark green, waxy area under the skin amounting to 10 to 20% of their volume on the side opposite the open face, and when examined under magnification, this dark green material had obviously shrunk excessively and thawed before it dried. Very little shrinkage was evident on the cooked peas. The raw peas had the texture of cooked peas on rehydration and they tasted very good. The consistency and flavor of the cooked peas was rather drab and they seemed to be over-cooked.

2. Fruits

a. Strawberries at 130° and 3.5 mm Hg seemed to freeze dry quite satisfactorily. These were the same sliced IQF strawberries that were used in the later larger scale runs and were supplied by a company which was freeze drying them. When the chamber pressure was raised to 8 mm Hg, heptane was seen to condense on the fruit so that the fruit temperature must have been about 20° (vapor pressure of heptane at 20° is approximately 8 mm). At this temperature the fruit would be partially thawed.

b. Apples at 150° and 3.5 mm Hg shrank badly and obviously thawed during drying. However, they did rehydrate readily to a rather soggy state having a very pleasant taste and odor. The dried material might very well be a satisfactory product.

c. Pears behaved quite similarly to the apples.

d. Quite a few attempts were made to freeze dry peaches and they were all unsuccessful. Fresh peaches cut into cubes, quick frozen, and dried in this apparatus shrank badly and obviously melted. Again however, the dried product rehydrated readily to give a material having somewhat the consistency of stewed fruit and a very pleasant taste.

Peaches purchased for the larger scale runs, Rio Oso Gems, sliced, sulfited, treated with ascorbic acid and IQF frozen also shrank badly in every case. Under the mildest conditions possible with this LPCS apparatus (100° and 3.5 mm Hg) and even with vacuum freeze drying at 100° and 50 microns these samples melted and shrank, so the poor results are quite likely the fault of the sample itself. Thawing and refreezing before drying reduced the shrinkage and seemed to improve the product even though the product was shrunken enough so that drying had obviously not occurred from the solid state.

3. Meats

a. Beef, raw

Several different samples cut or ground to various sizes were dried at 6 mm Hg and 150° to give products that rehydrated readily and had a good flavor and consistency. However, pieces larger than 1/4 or 3/8 inch were dark red and shrunken on the inside even though the outside of the piece retained its original size and shape. Apparently after the ice core retreated 1 to 3 mm from the surface the inside of the particle thawed.

b. Beef, cooked

The several samples of cooked beef apparently freeze dried satisfactorily by the LPCS procedure. The fat appeared to have melted however, and in some cases it soaked into the dried meat to some extent. Furthermore, the foreign taste suggestive of a hydrocarbon was apparent in many of the samples.

c. Chicken, cooked, white meat

This material gave every indication of truly freeze drying and of being a satisfactory product with the possible exception of a foreign taste due to absorption of carrier fluid.

d. Chicken, cooked, dark meat

This meat also freeze dried by the LPCS method but again the fat tended to melt into the dry meat. No off taste was observed in the dried dark meat.

4. Fish

a. Shrimp, raw, peeled

These darkened considerably and shrank slightly on drying but the product rehydrated readily and tasted very good.

b. Shrimp, cooked, peeled

These gave every indication of freeze drying very well and the product had excellent taste and consistency.

c. Halibut, raw

True freeze drying occurred with LPCS and the product appeared to be satisfactory although it was rather tough. Insufficient cooking may have been responsible for the toughness.

d. Rock cod

No shrinkage was evident.

e. Ling cod

This material freeze dried satisfactorily but it did retain a rather fishy odor which seemed to be particularly apparent in the streaks of dark meat.

To summarize the results from these preliminary trials, the LPCS procedure freeze dried cooked beef, chicken, fish and shrimp at 150° and 6 mm Hg without any melting, but raw beef thawed if the pieces were larger than about 1/4 inch.

Among vegetables only the leafy ones such as spinach and broccoli or those with rather a coarse structure like potatoes freeze dried. The skins of corn kernels, peas, and the dense cell structure of carrots impede the diffusion of water vapor from inside the sample to the extent that the partial pressure of water gets high enough for melting to occur.

Among fruits, only strawberries freeze dried and all the other samples shrank badly. However, these dried shrunken fruits had an open enough structure to rehydrate readily and give products that might very well be satisfactory.

III. PROCESS AND OPERATING VARIABLES

A. Measurement of Drying Rate

Since the rate or time of freeze drying is the principal dependent variable of interest, considerable effort was devoted to making this measurement in a stream of carrier gas and at low pressure. Two methods were evolved. The first measured the drying rate directly from the dew point of water in the carrier vapor; the second followed the weight of the sample as a function of time, and this proved to be the most useful and expedient of the two procedures.

1. Drying Rate From the Dew Point of Water

To follow the drying rate, the dew (or frost) point of water in the gas leaving the drying chamber can be determined. Figure II-1 shows the installation of the dew point tester (Cenco No. 35210). By having the pressure in the dew point chamber slightly below that in the drying chamber as indicated by an oil manometer (DPI 2) some of the vapors flow past the mirror in the dew point unit. The mirror is slowly cooled by liquid carbon dioxide and it is so arranged that a thermometer indicates the temperature of its surface. The temperature at which small ice crystals are first seen to form on the mirror is taken as the dew point of water.

With a noncondensable carrier gas it is quite easy to measure the dew point of water down to temperatures as low as -60°F, but with heptane condensing at about 10°F (under five to six millimeters of mercury) it is much more difficult to see when water first crystalizes. However,

reliable results appear to be possible by mounting a microscope to observe the mirror at five to ten magnifications and by cementing a very small boiling chip on to the mirror to nucleate the water vapor when it becomes saturated. Condensation of water is indicated by a stream of droplets or ice crystals falling from the nucleating site, through the film of heptane coating the mirror. From the dew point of the moisture, the partial pressure of water vapor leaving the drying chamber can be determined, and knowing the total pressure and rate of flow of carrier vapor (which is practically the only other gas present) the rate of flow of water can be calculated. This is the drying rate, if the carrier entering the system contains no water. Table III-1 shows a sample calculation and the results from one run.

In Table III-1 the instantaneous drying rates seem somewhat higher than they should be from the over all average rate based on the weight loss of the sample. Lack of precision in measuring both the flow of vapor and the pressure in the sample chamber are likely causes of this discrepancy.

It is interesting to compare this drying rate with that calculated from the drop in temperature of the carrier gas flowing through the bed. If the change in enthalpy of the water vapor all comes from "sensible heat" in the carrier gas:

a. Heat capacity of heptane vapor - .42 BTU/#-°F

b. Flow of heptane - 22 grams/minute

c. ΔH of water from ice at 30° to vapor at 150° = 1272 BTU/#

d. Temperature drop of heptane through bed at 20 minute time - 66°F

e. Drying rate = $\frac{22\ (.42)\ 66}{1272}$ = .48 gms. water/minute

This compares to .57 grams per minute from the dew point measurement.

2. Drying rate from loss in weight

A simple means was devised to follow the weight of a sample as it dried under LPCS conditions. A glass tube loaded with lead shot in one end floated vertically in a larger tube containing concentrated sulphuric acid. The sample of frozen food was supported on a screen mounted at the top of the floating glass tube. With this assembly (see Figure III-1) contained in the four inch LPCS apparatus, the loss in weight of the sample could be followed as it dried by noting the vertical position of the floating tube with a cathetometer. The float was calibrated between runs to relate its position to sample weight. The plastic screen which supported the sample was about 2-1/4" OD, and the funnel above it from which the carrier vapors were directed on to the sample had a throat diameter of 1-1/2".

The current of carrier vapor impinging on the sample caused the floating tube to oscillate slowly up and down, but the rather viscous liquid

TABLE III-1

DRYING RATE DATA

Run 47. Fish, Rock Cod, raw, 1/2" cubes, approximate.

Total time - 195 min.

Water evaporated - 27.9 grams from 37.7 grams sample.

Flow of Heptane, from rotameter, 32 cc/min or .218 gm mole/min.

Total pressure - 6.0 mm Hg.

Time Min.	Dew Pt. °F.	ΔP ** mm oil (SG .8)	Partial Pressure of Water mm Hg	Pressure in Dew Pt. Chamber mm Hg	Mole fraction of Water Vapor	Drying* Rate gm/min.
20	-5	5	.73	5.7	.128	.57
45	-10	3	.56	5.8	.097	.42
100	-18	4	.36	5.8	.062	.26
120	-19	4	.34	5.8	.059	.24
135	-20	4	.32	5.8	.055	.23
150	-25	4	.24	5.8	.041	.17
170	-40	4	.10	5.8	.017	.07

* Drying rate at 45 minutes

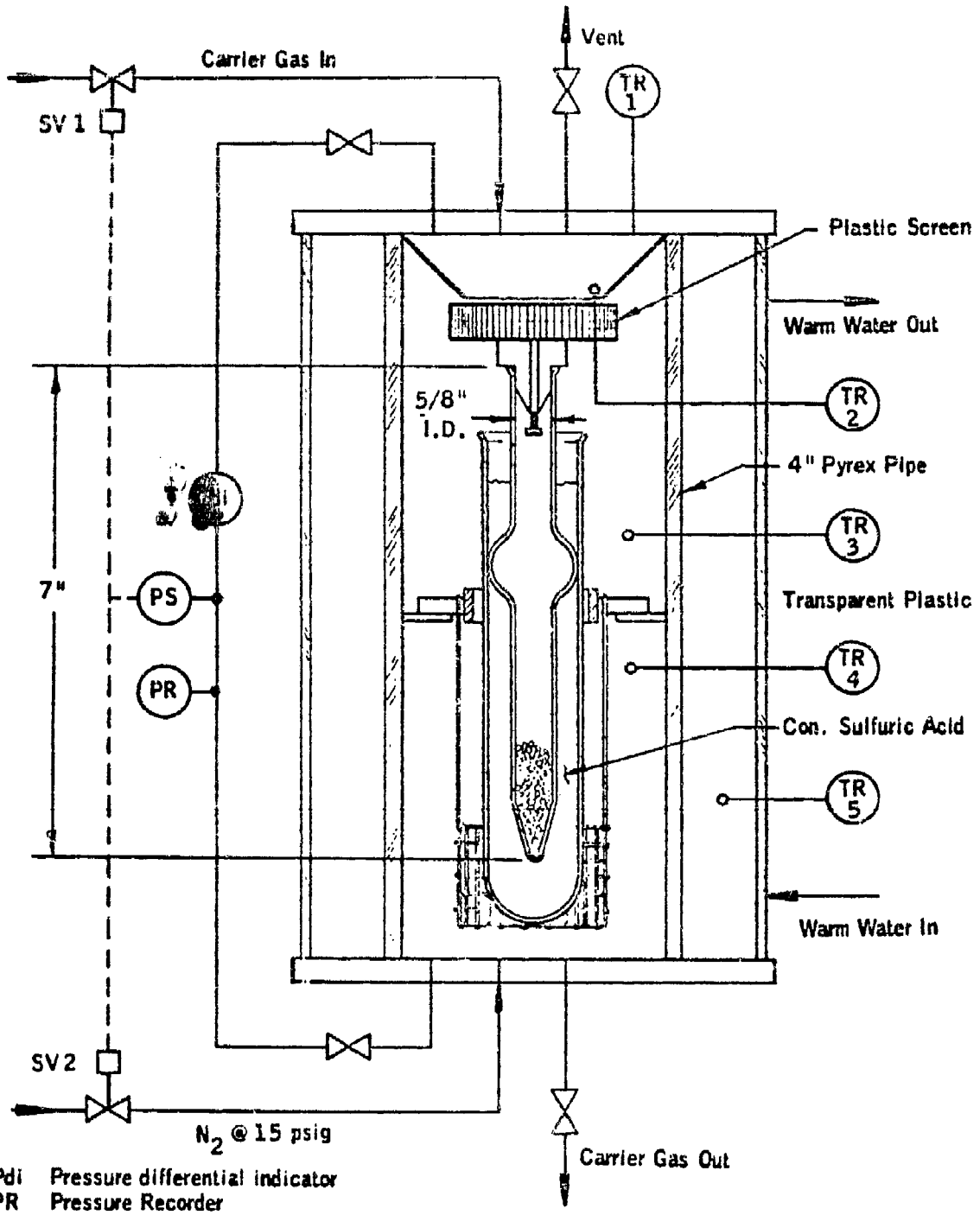
= (Total moles/min.) (mol. wt. H_2O) (mol. fraction H_2O)

$$= \frac{0.218}{(1 - 0.097)} \quad (18)\ (0.097) = 0.42 \text{ gms water evap./min.}$$

** Pressure difference between bottom of drying chamber and dew point apparatus.

Average drying rate, overall = (27.9 gm water)/195 min.

= 0.143 gm/min.



Pdi Pressure differential indicator
PR Pressure Recorder
PS Pressure Switch
TR Temperature Recorder
SV Solenoid Valve

FIGURE III-1 DRYING RATE APPARATUS

damped these oscillations and kept the frequency and amplitude low enough so that the cathetometer could readily observe the peak of each oscillation to within .05 millimeters. This apparatus provided a simple and reliable means to measure the weight of a sample inside the enclosing chamber and in the presence of a stream of carrier vapor. Its principal disadvantage was that high flows of vapor caused excessive oscillation and it was necessary to use a carrier flow such that a 7 gram sample losing weight by evaporation at 1% per minute would cause the average temperature of the vapor to decrease about 25°F. Thus the temperature to which a sample drying rapidly was exposed was somewhat less than that of one drying more slowly, and this tended to compress the observed drying rates.

The drying rate turned out to be very nearly constant for the first 25 to 50 per cent loss in weight; and therefore, the slope of this linear portion of the weight time plot was taken as the drying rate and expressed as per cent loss of total sample weight per minute. A computer program was prepared to calculate the least squares slope of the weight-time data over the portion of the data taken to be linear. The 95 per cent confidence limits of this slope are a measure of the precision of the weight determinations and of the approach to a constant rate. Appendix IV presents these data as the computer prepared them. Figure III-2 shows a weight-time plot for Run 158 which was typical, with the calculated straight line drawn through those points from which its slope was determined.

The intention in designing this apparatus was to make the flow of carrier vapor sufficiently large so that its change in temperature would be negligible and the sample would therefore dry under constant conditions. However, it turned out that excessive flows of carrier fluid caused too much oscillation and the sensitivity of the cathetometer was such that the precision of the weight determination suffered for samples smaller than about 3 grams. The first work with this apparatus used samples of 7 grams and the later runs used 3 gram samples.

The drying rate was very nearly constant in every case until the sample lost from 25 to as much as 50 per cent of its weight. This initially constant rate was particularly apparent with the 7 gram samples. The reason for this behavior (and incidentally this constant initial drying rate is quite common in freeze drying) has been given considerable thought. In drying liquid water from porous materials the constant rate is generally thought to be caused by flow of water through the capillary structure of the solid to its outside surface, but in freeze drying the moisture is not free to move.

If during a considerable portion of the drying cycle the thermal resistance of the dried shell of food around the ice core is small compared to the resistance to transfer of heat through the boundary layer surrounding the particle, the drying rate would be constant. Accordingly the model proposed by Ginnette and co-workers (4) whereby the drying rate is determined by the transfer of heat from the surroundings through the boundary layer of a spherical food particle, then through the dried

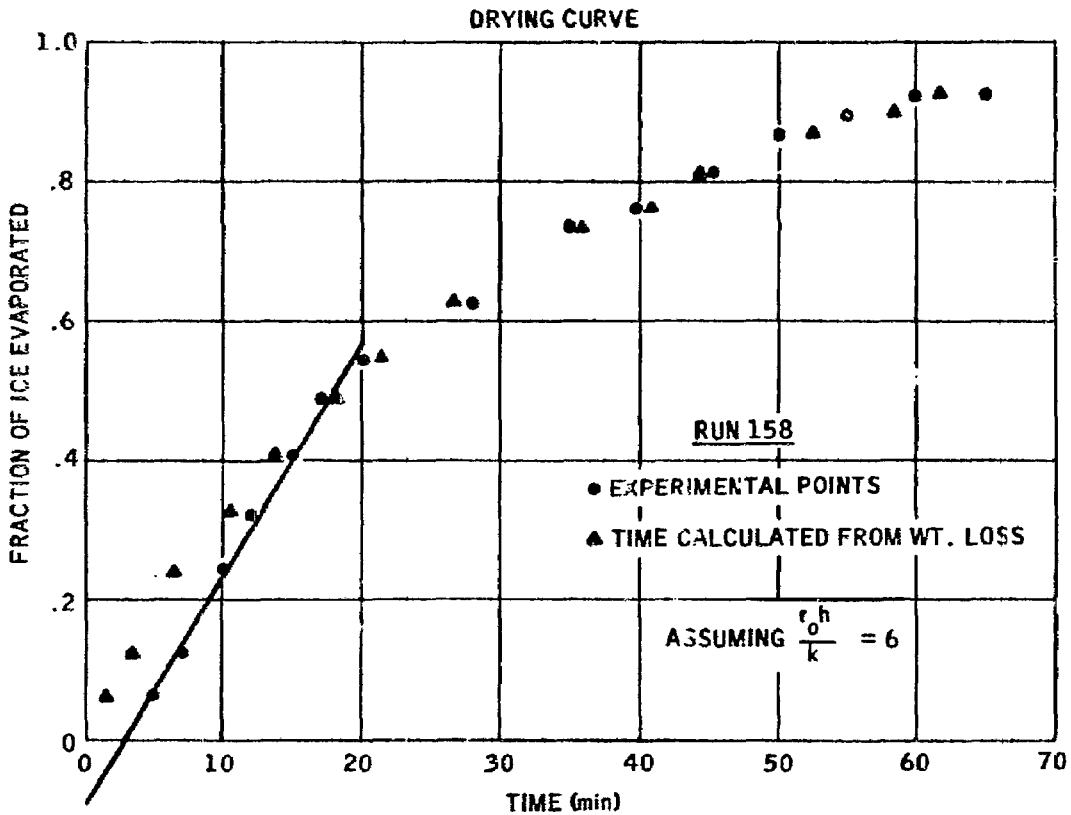

DRYING CURVE
FRACTION OF ICE EVAPORATED
1.0
.8
.6
.4
.2
0
0
10
20
30
40
50
60
70
TIME (min)
RUN 158
● EXPERIMENTAL POINTS
▲ TIME CALCULATED FROM WT. LOSS
ASSUMING $\frac{r_o h}{k} = 6$

FIG. III-2

shell around the ice core was used. From this model the drying time can be shown to equal:

$$\theta = \frac{\Delta H \, \Delta\rho \, r_o}{3(T_p - T)} \left[\left(\frac{r_o}{2k} + \frac{1}{h}\right) + \left(\frac{r_o}{k} - \frac{1}{h}\right) y - \frac{3}{2} \frac{r_o}{k} y^{2/3}\right]$$

T_p is the constant temperature of the gas stream, T the temperature of the ice core, ΔH the change in enthalpy of water from ice to vapor, $\Delta\rho$ the change in density of the food before and after drying, r_o the radius of a spherical food particle, k is the thermal conductivity of the dried food, and h is the film coefficient for transfer of heat through the boundary layer. Also, y is the fraction of moisture remaining in the sample at time θ. The princip ' assumption involved in this derivation is that $(T_p - T)$ is constant and since T_p is approximately 150° and T only varies between 15° and 30°F the assumption seems justified. Appendix II-A shows the derivation of the above expression in detail. It is interesting to note that if r_o is taken as half of the edge distance of a cubicle food particle the same expression results.

By trying various ratios of h to k/r_o a value was found which gave the calculated points shown in Figure III-2. The experimental point at 23 minutes was used to evaluate the constant and the value of 6 was used for $h/k/r_o$. If k is equal to .020 BTU/ (°F - hour - foot), estimated from Harper's work (5) and using 3/8" cubes, the film coefficient h turns out to be 8 BTU/ (hour-square foot -°F). This compares to a value of 3.2 calculated from a generalized correlation in Appendix II-D.

In figure III-2 the agreement between experimental and calculated points is good except during the first 10 to 15 minutes of the drying period, and it may be that the disturbances caused by starting the apparatus persisted for this long.

At any rate, boundary layer resistance to the transfer of heat from the gas stream to the ice core must be significant for food particles of this size. Initially Figure III-2 shows the calculated rate to be higher than the experimental one, which could be caused by the samples being colder at first than the ice core temperature which developed as the drying proceeded. If the samples started out somewhat colder than the steady state drying temperature, then the rate of drying while slower initially would not tend to fall off sharply as drying proceeded since the ice core temperature would be rising to its steady state value. This could be the course of events which Figure III-2 shows for Run 158. Thus the constant initial rate may be caused by two offsetting effects: first the very slowly decreasing rate initially due to the thermal resistance of the boundary layer and second the tendency of the rising ice core temperature to increase the drying rate.

It might be well to point out that where the thermal resistance of the boundary layer is negligible, the ice core temperature should be constant as drying proceeds, but when T_o, the temperature of the outside particle, rises during drying, the ice core should slowly increase in temperature also. Appendix II-C gives the detailed reasoning on which these statements are based. Therefore in the runs discussed here the inside

temperature determined by the steady state transfer of heat to the ice core and diffusion of water vapor away from it should slowly increase as drying proceeds.

It is also worthwhile to note that the film coefficient, h, for heat transfer through the boundary layer surrounding these particles should be independent of pressure and only weakly dependent on temperature (see Appendix II-D). For both laminar and turbulent flow, the film coefficient depends primarily on the heat capacity of the fluid and its mass velocity, both of which are constant with pressure if the mass flow rate does not vary. The film coefficient would be proportional to the mass velocity (mass flow per unit time per unit area) to the .7 power which is in turn the product of the density and the average velocity.

Except where noted all the weight-time drying runs reported here used a flow of 11 cc per minute of liquid heptane and thus the mass velocity was the same for all the pressures and temperatures, and the film coefficient should have been very nearly the same in every run. If 11 cc per minute of liquid heptane (measured as liquid) flows as vapor in a jet 1-1/2" in diameter as shown in Figure III-1 past 3/8" particles, the Reynolds number would be about 150, and this is in the upper range for laminar flow (6).

From the above analysis of the weight-time data to be presented here, the use of rates based on the slope of the initial straight line portion of the plot may appear somewhat questionable. Therefore drying rates are also reported based on the slopes of the weight-time plots at a point where 60% of the water has evaporated and where the insulating dried shell of material surrounding the ice core should be well developed. In this way the drying rate becomes more dependent on the properties of the dried food and of the gasses filling its pores and somewhat less dependent on its external contact with the carrier gas stream. However, either method of determining the drying rate leads to the same conclusions, as does the drying time which is arbitrarily taken to be the time required to reach the final constant weight for 15 minutes.

B. Flow of Carrier Vapor

1. Functions of the Carrier Vapor

The carrier vapor performs three principal functions:

a. It increases the effective thermal conductivity of the dried food surrounding the ice core of a particle.

b. It sweeps water away from the outside of the drying particles.

c. It transfers heat by convection to the particles.

The work of Harper (5) has shown that pressures of 2 to 5 mm Hg of heavier gasses are required to significantly increase the thermal conductivity of

freeze-dried foods over what they are at essentially zero pressure. One of the most worthwhile functions of the carrier vapor is to raise the thermal conductivity of this insulating layer so that heat can be transferred faster to the ice core.

Since water vapor diffuses from the ice core to the outside of a drying food particle by means of a gradient in its partial pressure, the partial pressure of water vapor surrounding the food particles must be kept low, actually well below the equilibrium value corresponding to the maximum ice core temperature for the food under consideration. This temperature may vary from 30°F down to 0° or below for foods with a high sugar content. Therefore the partial pressure of water vapor surrounding the food particle must be less than about 1 millimeter for effective drying to take place.

A fourth effect of the carrier fluid might be mentioned - impeding the diffusion of water vapor from the ice core to the outside of the food particle. This mass transfer must take place by molecular diffusion and it must be rapid enough to prevent the pressure of water at the ice core from exceeding that corresponding to equilibrium at the temperature of fusion.

If the total pressure is 5 millimeters and the maximum partial pressure of water is 1 millimeter, the flow of carrier must be at least four times that of water vapor leaving the apparatus (on a molal basis).

If the carrier vapor supplies sensible heat to the food particles, the amount of heat transferred by convection is a function of carrier flow. For instance, if the carrier is heptane and its temperature decreases 100°F in flowing through a bed of food, about 5.8 moles of carrier will be needed for every mole of water evaporated. Since a temperature drop of 100°F is large and more flow would be needed for a lower temperature drop, the minimum flow of carrier is most likely to be dictated by the need to carry heat to a bed of drying food. Thus, the flow of carrier fluid can only be minimized if it is somehow reheated as it passes through a bed of food.

2. Effect of Carrier Flow on Drying Rate

Carrier flow affects the drying rate in two ways:

a. By transfer of heat to the bed of food.

b. By the heat transfer characteristics of the boundary layer of gas surrounding each food particle.

It has already been shown that the boundary layer resistance to heat transfer is likely to be very significant for food particles under about 1/2" and also that this resistance is independent of pressure at a given mass flow rate, but that it varies inversely as the .7 power of the mass velocity (fluid density times its average velocity). Thus, the drying rate should increase significantly with the mass flow of carrier if all other conditions are held the same. Table III-2 shows the initial drying rate for several different mass flow

TABLE III-2

EFFECT OF CARRIER FLOW ON DRYING RATE

Sample: Beef, lean, cooked. Diced 3/8" x 1/4" x 1/4"
(approx. 3 grams)

Run	Temp. °F	Press. mm Hg	Heptane Flow cc/min.	Drying Rate %/min.	Confidence Limits + %/min.
116	150°	10	3.3	1.18	.09
118	150°	10	11.2	1.36	.17
122	150°	10	11.2	2.04	.13
117	150°	10	7.2	1.47	.63

rates of heptane past 3 gram samples in the weight-time apparatus. The increase in drying rate is much less than might be expected and the probable reason is that radiation contributes significantly to the transfer of heat to the outside of the particle in this apparatus.

For a 3/8" cube drying at 2% per minute about 40% of the heat should be transferred to it by radiation if its external temperature is 30°F. The actual external temperature is probably quite a bit above this but the influence of radiation is nevertheless probably significant.

In a bed of food over 1 or 2 inches deep the surface available to accept heat transferred by radiation would be small and it would be necessary to transfer practically all of the heat by convection.

C. Depth of Bed

The principal influence of bed depth on drying rate is in its effect on the exchange of heat and mass between the food and carrier fluid. A deeper bed allows the carrier to transfer a larger amount of sensible heat to the food and to become more nearly saturated with water vapor and the price for this better mass and heat transfer is of course paid in drying time. All the food in a bed must be exposed to the drying conditions until the bottom or the last piece of food is dried.

It is theoretically possible for the carrier fluid to approach a steady state "wet bulb" temperature if it is to flow through a deep enough bed of frozen food so the temperature of the vapor approaches that of the food. If the food is not to thaw at this temperature the flow of vapor must be sufficient to keep the partial pressure of water vapor below the saturation pressure at the desired freezing point of the food.

In an actual case the maximum temperature drop of the vapor flowing through a given bed is a function of the flow rate, particle size, and bed depth, and in none of this experimental work was the bed sufficiently deep for the temperature of the carrier fluid to approach that of the food.

Figure III-3 shows a typical temperature recording (Run 72) for a bed of 1/4" fish dices, 3" deep. Here the carrier temperature going into the bed is about 140° while the temperature of the vapor leaving the bed rises from 50° to almost 140° as the drying proceeds. The temperature inside undried food particles stays below the freezing point until the food pieces are practically dry. In Figure III-3 the indicated temperatures of the food particles very quickly rise above 30°F, but these are undoubtedly too high since the thermocouple wire can conduct heat into the junction when the temperature varies sharply along the wire. In every instance where pieces of partially dried fish were examined, their ice core was found to be well frozen even though particle temperatures indicated were much higher than 30°.

It should be emphasized that the thermal history of particles varies with their position in the bed. Those at the top of the bed are dried first and are then exposed to the carrier gas temperature until the bottom pieces are dried. Pieces on the bottom are exposed to gradually increasing carrier temperatures as they dry.

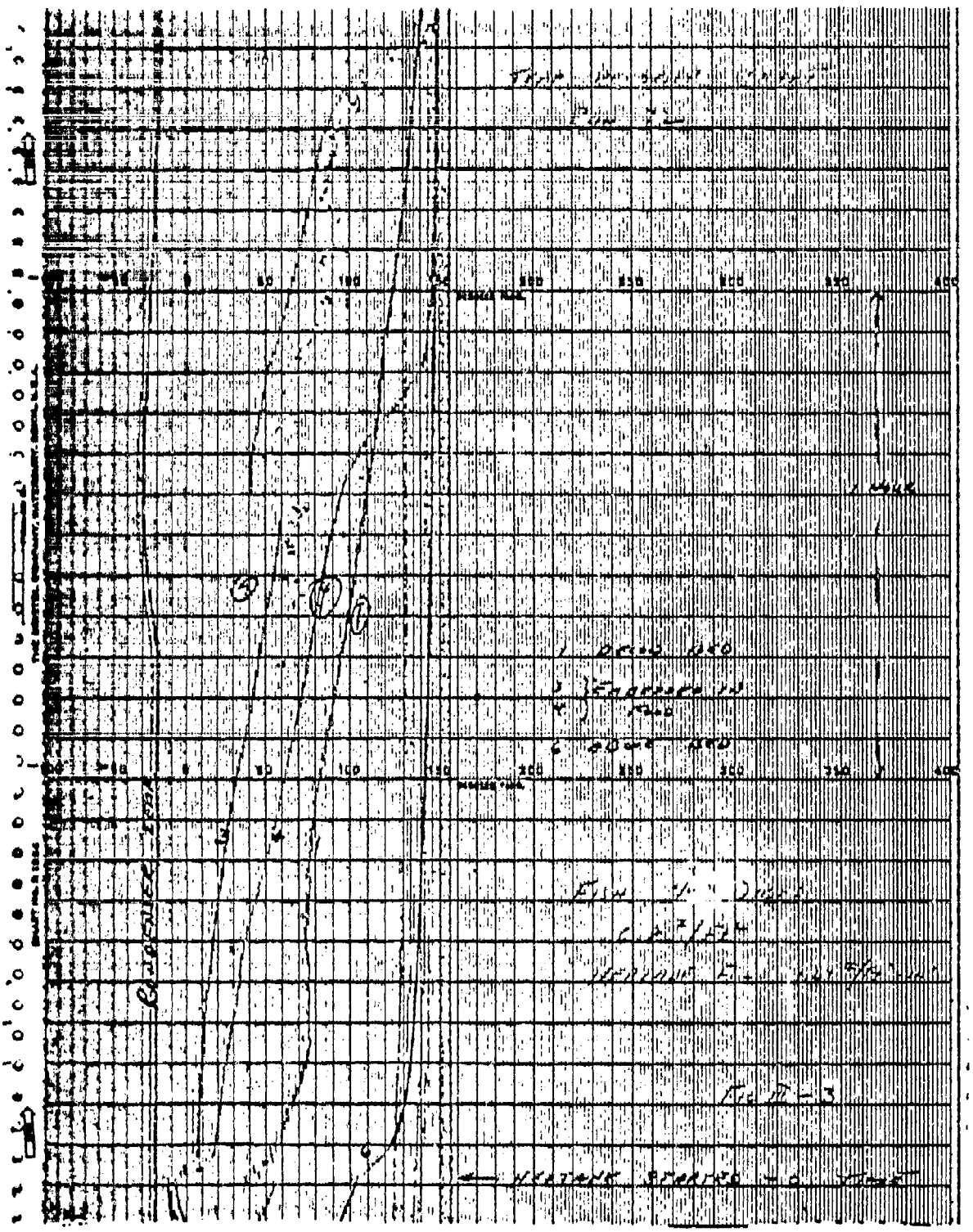


FIGURE III-3 RUN 72 — FISH, 1/4" DICES

D. Size and Shape of Food Pieces

For the transfer of heat and mass through the dried shell of food surrounding the ice core, the drying rate is inversely proportional to the radius squared for spherical particles (see Appendix II-A). On the other hand, the rates of heat and mass transfer through the boundary layer are inversely proportional to the radius alone. Therefore the actual over all rate varies approximately as one over the radius to a power somewhat less than 2.

In the various apparatus used in this work, however, faster drying cooled the carrier gas to a greater extent and therefore the driving force for transferring heat or mass was lower at higher drying rates or for smaller particles and this effect would tend to reduce the observed influence of particle size on the drying rate. Figures III-4 and III-5 and Table III-3 show the influence of particle size on the drying rate for fish, raw beef, peas, corn and strawberries. As would be expected the drying rates were higher for smaller particles and the drying times were shorter. The data in Figures III-4 and III-5 were calculated from dew point measurements and those in Table III-3 from the weight-time plots.

Obviously, as particle size increases, the internal resistance to the transfer of heat and mass outweighs the resistance of the boundary layer, but below 1/2" the boundary layer resistance appears appreciable.

The structure of the larger pieces of dried beef was rather peculiar in that the outer millimeter or so was very porous and had definitely freeze dried, while the centers of the particles appeared to have thawed before they dried, as there were large voids in the tissues and the meat fibers had a shrunken, congealed appearance. Here the temperature at the center of the particle must very definitely have increased as the drying progressed. The smallest pieces (1/4" cubes) of raw beef appeared to have dried completely from the frozen state.

All the fish samples freeze dried without difficulty, as indicated by the lack of shrinkage in the dried product and also by the fact that the ice cores were well frozen in several samples which were interrupted before drying was complete.

Peas and corn, however, presented complications in freeze drying. Peas, which had been merely scarified by cutting their skin, definitely thawed before they were completely dry at 150° and 6 millimeters. Cutting the peas in half reduced the extent of thawing considerably and those that were crushed before freeze drying gave no evidence of thawing.

Whole kernel corn, as cut from the cob, also thawed while drying although the product rehydrated quite readily. Cutting the kernels in half, however, gave a dried product which had shrunken very little inside the skin. Thus with foods enclosed by a skin such as peas and whole kernel corn, it appears necessary to provide a large opening in the skin by cutting the particle in half to allow the water vapor to diffuse out without building up a partial pressure sufficient to cause fusion.

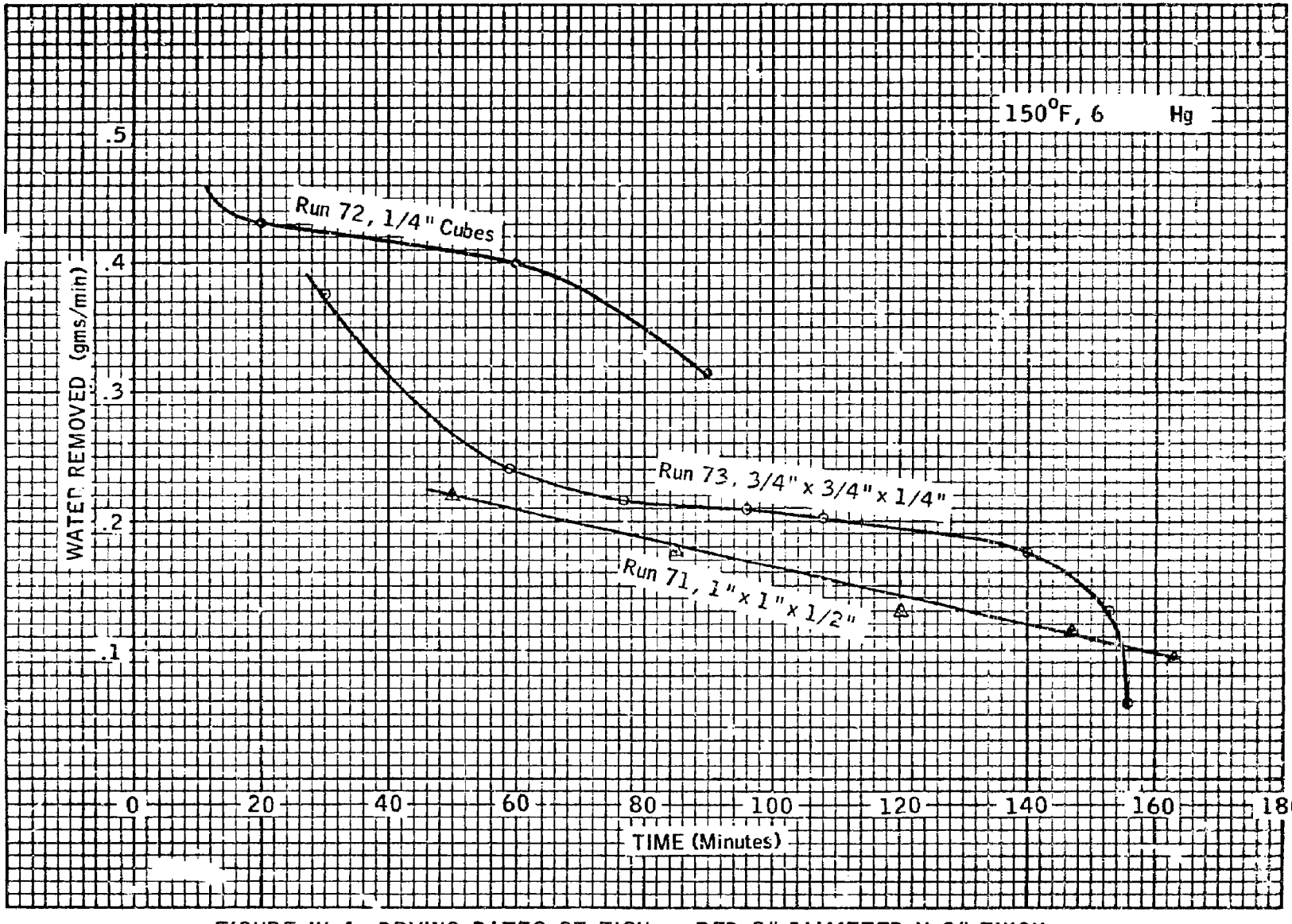


FIGURE III-4 DRYING RATES OF FISH — BED 2" DIAMETER X 3" THICK

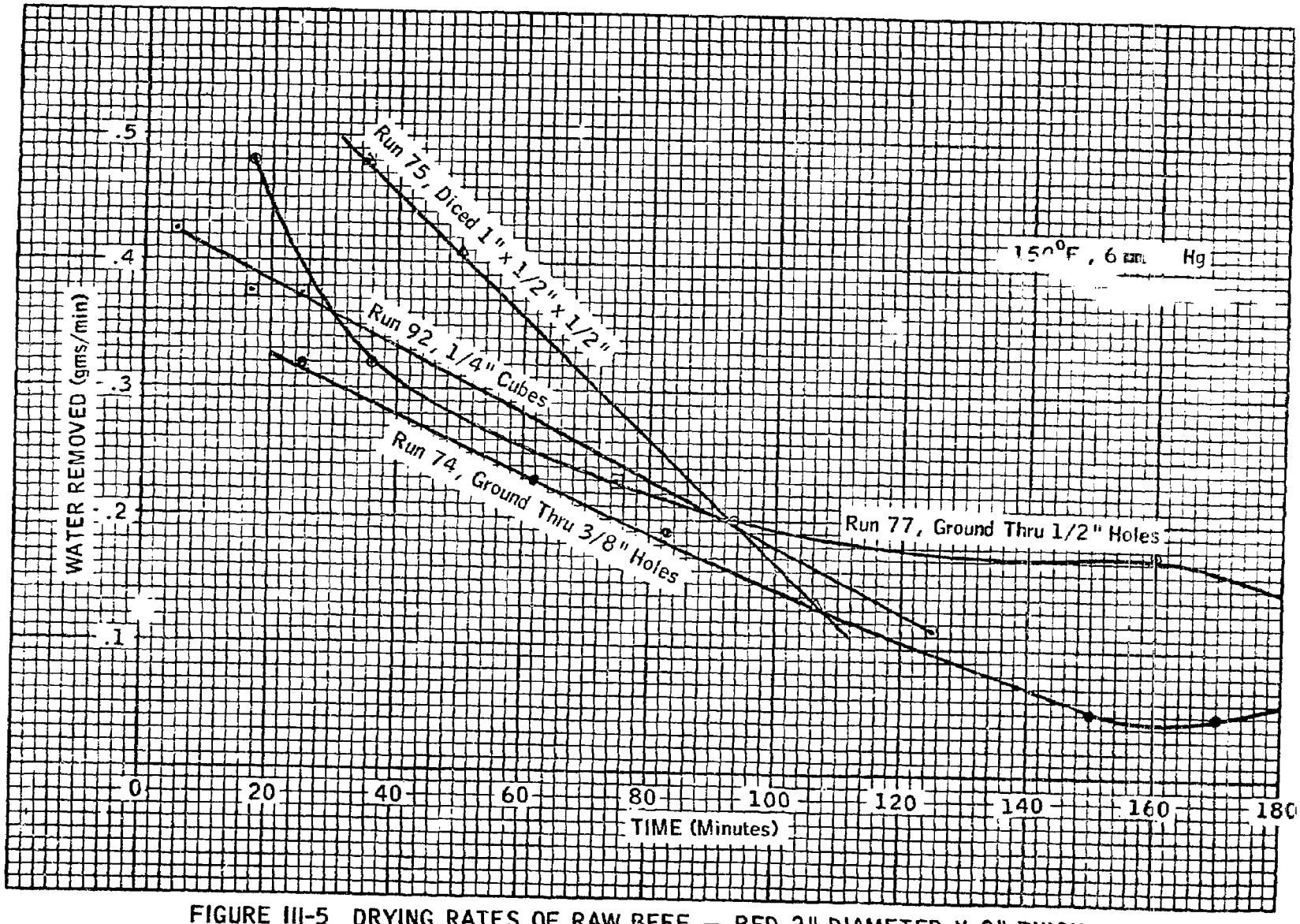


FIGURE III-5 DRYING RATES OF RAW BEEF — BED 2" DIAMETER X 3" THICK

E. Effect of the Carrier Temperature

Obviously, the higher the temperature of the carrier vapor the faster the drying rate, but the temperature is limited by either that where the food is scorched or where the ice core melts.

If heat is transferred to the frozen particle more rapidly, water vapor is evolved more rapidly and for this diffuse through the dried layers of food, the driving force or partial pressure of water vapor next to the ice core must rise. If the partial pressure of water vapor gets above about 4 mm Hg, the food melts; (if its fusion point is 30 F) so at given conditions the temperature of the carrier vapor may be limited by the tendency of the food to melt. The drying rate for a spherical food particle as calculated from mass transfer is:

$$\frac{dy}{d\theta} = \frac{-3(P-P_p)M}{R\Delta\rho r_0} \frac{1}{\left[\frac{T_0}{k_c} + \frac{T_{av} r_0}{D}\left(\frac{1}{y^{1/3}}-1\right)\right]}$$

and as calculated from heat transfer considerations the drying rate is:

$$\frac{dy}{d\theta} = \frac{-3(T_p-T)}{\Delta H \Delta\rho r_0} \frac{1}{\left[\frac{1}{h} + \frac{r_0}{k}\left(\frac{1}{y^{1/3}}-1\right)\right]}$$

These expressions are derived in Appendix II-A and II-B, and the expression for the mass transfer assumes that the partial pressure of the carrier is several times that of water vapor. When the temperature of the ice core is fairly steady these expressions can be equated to give the following:

$$\frac{(T_p-T)}{(P-P_p)} = \frac{\Delta H}{R} \frac{\left[\frac{1}{h} - \frac{r_0}{k}\left(\frac{1}{y^{1/3}}-1\right)\right]}{\left[\frac{T_0}{k_c} + \frac{r_0 T_{av}}{D}\left(\frac{1}{y^{1/3}}-1\right)\right]}$$

If the two terms in brackets are proportional to each other, then the ratio of the temperature difference and the pressure difference should be constant and therefore the ice core temperature should be constant as y varies or as drying proceeds (see Appendix II-C). However, there is no reason why the bracketed terms should be equal or proportional, and in general they would not be, so therefore the ice core temperature can be expected to vary somewhat as drying proceeds.

The effective diffusivity of the dried food, D, would depend to a considerable extent on the distribution of pore sizes whereas the thermal conductivity, k, would be a function of the porosity but should not be greatly affected by the size of the pores. Since the effect of the carrier vapor is to increase k and decrease D, food is much more likely to melt when being freeze dried with the carrier gas than it is in normal vacuum freeze drying. In vacuum freeze drying water moves out of the food by bulk flow whereas in the LPCS process water is transported by molecular diffusion, and for a given rate of mass transfer or drying rate this requires a larger driving force and therefore a larger pressure of water vapor adjacent to the ice core.

Therefore products needing particularly low ice core temperatures are not suitable for the LPCS process. For example, peaches, with a high sugar content, and also those foods with a pore structure of low permeability such as carrots would be unsuitable for this process.

F. Effect of Pressure

In the original LPCS concept (FMC proposal No. P-2027) the drying rate was postulated to be a maximum at about 10 millimeters of mercury. The thermal conductivity of an ideal gas is independent of pressure but the contribution of a permeating gas to the thermal conductivity of a porous solid is negligible if the pore size averages much below the mean free path of the gas. Thus the gas pressure must build up to the point where its mean free path is significantly less than the average pore size before the gas can contribute to the conduction of heat through a solid, and with a wide variety of gasses this build up occurs at pressures between from 1 to 10 millimeters (5).

Likewise the diffusivity of an ideal gas is inversely proportional to the pressure, but the mean free path must be quite a bit less than the pore size before the carrier gas will interfere with diffusion of water vapor through a porous food particle. Thus there should be an inert or carrier gas pressure such that the thermal conductivity has been raised significantly over its value in vacuum, and yet not so high that the diffusivity of water vapor has been unduly reduced. This optimum pressure is in the range of 5 to 15 millimeters.

As pressure increases, however, two other considerations arise which may make it impossible to attain the maximum. First, as pressure and therefore the thermal conductivity of the dried food rises, heat is transferred to the ice core more rapidly, and moisture must diffuse more rapidly from it, both of which cause the ice core temperature to rise; and if it goes above the point where significant fusion occurs, freeze drying will no longer take place. The second consideration, with a condensible carrier vapor, is that the pressure may rise to the point where carrier vapor will condense on the ice core of the food. For instance, at 30°F the vapor pressure of normal heptane is about 11 millimeters, and that of water is about 4 millimeters; so that with a total pressure over 15 mm Hg either heptane should condense on the ice core or the temperature of the ice core will rise above 30°F thus thawing the food.

At a total pressure of 8 millimeters, heptane was observed to condense on a freeze-drying strawberry. Due to their high sugar content, strawberries thaw at temperatures considerably below 30°F and apparently where heptane would condense at 8 millimeters. The strawberries subsequently thawed, during drying.

Drying rates were determined over a wide range of pressures with 1/4 to 3/8" cubes of lean, cooked beef in an effort to verify the optimum drying rate experimentally. Table III-4 and Figures III-6 and III-7 show the results of this effort. Approximately 3 gram samples of the cooked beef, which included 5 or 6 dices, were dried in the weight-time apparatus described previously. Drying rates, when 60% of the moisture had been evaporated,

TABLE III - 3

VARIATION OF DRYING RATE WITH PARTICLE SIZE AND SHAPE

(Samples 7.0 ± 0.3 grams)

Run	Particle size and shape	Temp. °F	Press. mm Hg	Drying Rate %/min.	Initial 60% dry	Confidence Limits %/min.	Drying Time, min.
	FISH, LING COD FILLETS						
90	1/2" x 1/4" x 1/4", 7 pieces	150	6	.71	.54	0.04	195
91	3/4" x 1/2" x 1/2", 2 pieces			.53	.34	0.03	245
89	1" x 3/4" x 3/4", 1 piece			.41	.30	0.03	>260
	BEEF, RAW, LEAN						
85	Diced, 1 /4"	150	6	.78	.73	0.03	200
88	Diced, 1/2", 4 pieces			.61	.50	0.03	205
82	Diced, 1" x 3/4" x 1/3", 2 pieces			.59	.39	0.04	
83	Ground through 1/2" holes approx. 3/8" x 3/8" x 1/2", 4 pieces			.61	.45	0.04	218
84	Ground through 3/8" holes approx. 3/8" x 1/2" x 1/2", 3 pieces			.55	.31	0.04	240

Table III - 3

Run	Particle size and shape	Temp. °F	Press. mm Hg	Drying Rate %/min.	Initial 60% dry	Confidence Limits %/min.	Drying* Time, min.
	PEAS						
95	Cut in half, then crushed while frozen	150	6	1.10	.83	0.13	160
94	Cut in half			.86	.65	0.09	180
93	Scarified by cutting skin			.76	.71	0.03	178
	CORN CUT FROM COB						
97	Kernels cut in half	150	6	.92	.80	0.07	130
96	As cut from cob			.66	.55	0.05	175
	STRAWBERRIES, IQF, SLICED						
101	Cylinders 1/4" D x 3/8"	130	3.5	.92	.63	0.03	165
100	Cylinders 3/8" D x 3/8"			.74	.45	0.03	215
102	One slice 1" D x 3/8"			.56	.26	0.05	>300

*Drying time includes constant weight period of 15 minutes.

Table III - 3 (Cont'd)

TABLE III - 4

EFFECT OF PRESSURE AND TEMPERATURE ON DRYING RATE

Run	PRESS. mm Hg	DRYING RATE, %/min. @ 60% Dry	DRYING RATE, %/min. Initial Constant Rate		WT. LOSS @ Const. Rate %	DRYING TIME min.	MOISTURE CONTENT By Wt. Loss %	MOISTURE CONTENT By Drying Apparatus
			- - - - - 120° F - - - - -					
127	4	.62	1.57 ±	.17*	33**	105	59	56
131	4	.69	1.25	.35	31	110	64	56
132	6	.65	.84	.08	39	110	62	54
133	8	.82	1.11	.57	42	85	64	61
128	10	.79	1.06	.07	36	-	60	59
130	10	1.07	2.04	.86	33	105	64	57
164	10	1.42	1.87	.22	44	-	74	65
134	15	1.31	2.04	.86	33	85	62	63
165	15	1.15	2.30	.31	42	69	70	57
166	15	1.60	1.84	.23	48	73	63	57
129	19	1.27	1.81	.14	44	85	63	63
						Aver.	64	59
			- - - - - 150° F - - - - -					
120	4	.72	.67 ±	.61	27	75	61	48
121	4	.82	1.51	.21	34	75	62	48
158	5	.78	2.01	.22	33	75	61	56
124	8	1.05	1.49	.15	41	75	65	55
118	10	1.03	1.36	.17	40	70	63	51
122	10	1.59	2.04	.13	39	60	59	53
157	10	1.38	2.09	.27	39	68	63	62
123	15	1.20	1.89	.26	33	70	62	56
156	15	.83	1.13	.19	41	88	61	55
159	15	1.16	1.56	.25	44	60	66	61
160	15	1.23	1.79	.12	42	95	68	62
125	17	1.15	2.31	.38	35	65	62	59
119	19	1.68	2.17	.42	45	55	60	59
						Aver.	63	56

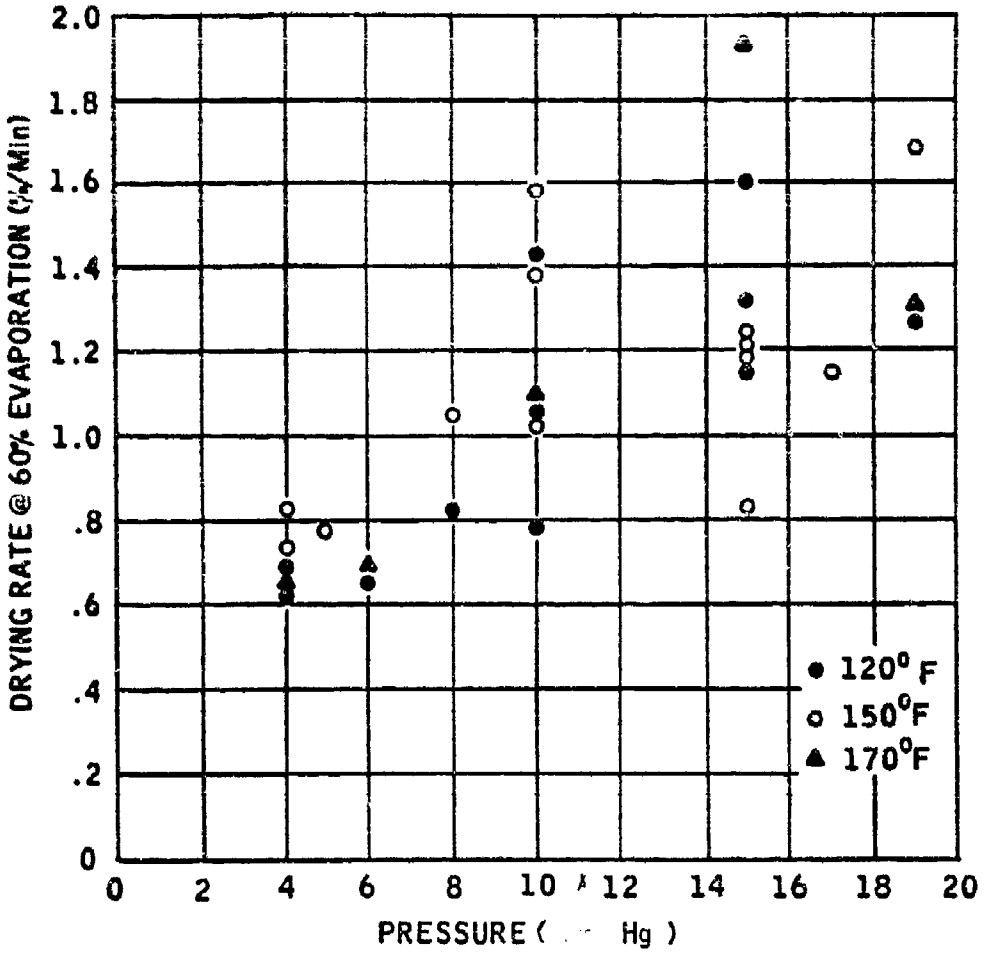
Table III - 4

Run	PRESS. mm Hg	--- DRYING RATE, %/min. --- @ 60% Dry	Initial Constant Rate	WT. LOSS @ Const.Rate %	DRYING TIME min.	-- MOISTURE CONTENT --- By Wt. Loss %	By Drying Apparatus
			---------- 170° F ----------				
136	4	.68	1.58 ± 1.00	37	70	65	50
139	6	.65	1.54 .25	26		61	59
138	10	1.09	1.40 .14	30		60	49
137	15	1.93	2.74 .40	40	65	61	63
140	19	1.23	1.65 .49	44	55	64	55
					Aver.	62	55
			------- HEXANE at 150° F ----				
144	8	1.05	1.55 ± .20	35	78	63	56
142	15	1.26	1.55 .16	39	80	62	63
147	20	1.02	1.43 .14	30	97	61	59
146	30	.96	1.47 .11	38	77	61	56
143	50	1.03	1.82 .40	37	82	63	61
					Aver.	62	59

* ± 95% Confidence Limits

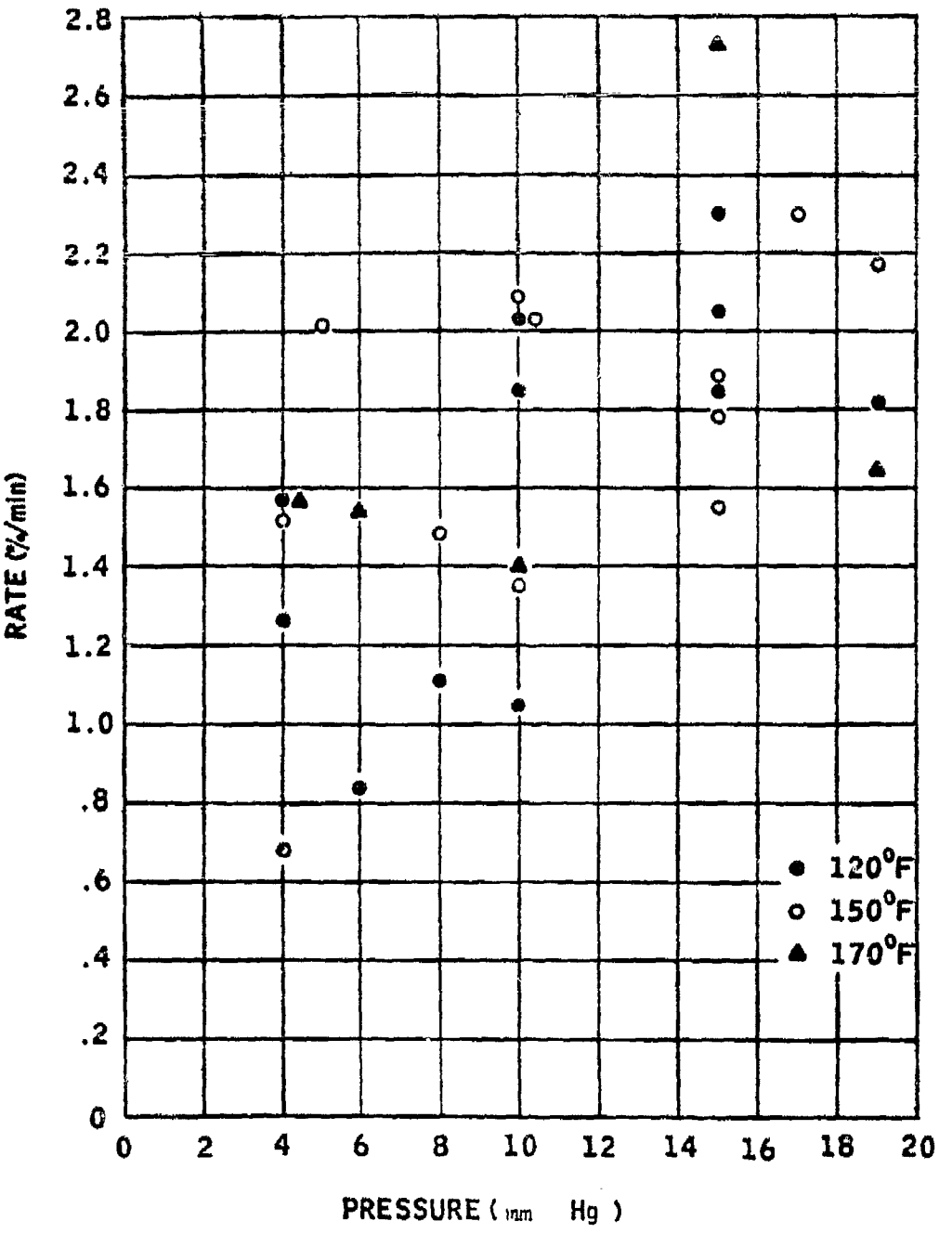
** Wt. Loss over which Drying Rate appeared to be constant.

Table III - 4 (Cont'd)



EFFECT OF PRESSURE AND
TEMPERATURE ON DRYING RATE
WITH 60% OF MOISTURE REMOVED —
COOKED BEEF, DICED

FIG. III-6



EFFECT OF PRESSURE AND
TEMPERATURE ON INITIAL DRYING RATE —
COOKED BEEF, DICED

FIG. III-7

and from the initial constant rate of drying, are tabulated in Table III-4; and while there is considerable scatter in the results, increased pressure does raise the rate of drying. Likewise, the drying times tabulated in Table III-4, which are the times required to attain a constant final weight for 15 minutes, generally decrease with rising pressure. Uncertainties in the measurements obscure an optimum pressure although Figures III-6 and III-7 may possibly show a maximum in the drying rate at 15 millimeters.

The effect of temperature is also not shown clearly by Figures III-6 and III-7, although as expected the rate does appear to be generally higher for the higher temperatures.

Probably the main reason for such poor reproducibility in these drying rate measurements is that the shape and size of the diced beef particles varied somewhat, and since only 5 or 6 particles were used in a drying run, the actual surface exposed to the drying atmosphere, as well as the texture of individual pieces was quite variable. Another source of error was the tendency of the floating tube in the drying apparatus to stick to the sides of the tube in which it floated. The apparatus was usually tapped before taking a reading to cause the float to assume its equilibrium position; but in the final stages of drying when the change in weight was very small the effect of this sticking may have been appreciable, and this is suggested by the fact that the moisture content indicated by the drying apparatus was generally lower than that determined by weighing the sample in and out (see Table III-4).

The detailed data from which Table III-4 and Figures III-6 and III-7 were prepared are presented in Appendix IV

The fact that heptane should condense on a frozen food particle if the pressure exceeded 15 millimeters has been noted. However, at 15 millimeters no condensation was observed. and it did not seem to occur even at 19 millimeters. The reason for this may be that the heptane used, which was of reagent grade, was actually a different isomer than that for which data were published (8). This material was a pure isomer as indicated by a single clearly defined peak on a gas chromatograph; and it apparently had a higher vapor pressure than the value cited from heptane in the literature. For example, at 6 millimeters normal heptane should have a dewpoint of 15°F, but in the dew point measurements, it was not observed to condense until the temperature had been lowered to 8 or 10°F, so that this particular heptane appears to be more volatile than that for which the data are given.

In an effort to extend the drying measurements to higher pressures where heptane would undoubtedly condense, several runs were made using hexane as a carrier fluid. Table III-4 shows these results for pressures of 8 to 50 millimeters, and strangely enough, pressure had very little effect on the drying rate over this range. Actually, Harper's calculations as shown in FMC-CEL Proposal #P2027 (7, 9) show a very flat maximum in the drying rate as a function of pressure and these data are probably not sufficiently precise to show a maximum effect conclusively.

The quality of the beef freeze dried under all these conditions appeared to be reasonably good. The cooked beef gave every indication of having freeze dried in every case, but the dried samples may have shown somewhat better water retention at the lower pressures. Table III-5 shows some data for these samples.

TABLE III - 5

EVALUATION OF COOKED BEEF DRIED BY LPCS

Run	Carrier	TEMP.	PRESS. mm Hg	MOISTURE %	RETENTION gms.H_2O/ 100 gms.	TASTE
164	HEPTANE	120°	10	7.0	95	Fair to good
165	"	120°	15	4.6	60	Fair
166	"	120°	15	5.8	81	Fair
158	"	150°	5	1.0	89	Good
157	"	150°	10	2.9	110	Fair - tough
156	"	150°	15	2.8	54	Fair - tough
159	"	150°	15	3.3	106	Foreign Taste - bad
160	"	150°	15	1.8	123	Slight foreign taste
138	"	170°	10			)Fair - Foreign
137	"	170°	15			) taste
144	HEXANE	150°	8		94	Fair
142	"		15		81	Very good
147	"		20		64	Good
146	"		30		80	Fair
143	"		50		68	Good

IV [illegible]

A. Food - Sources and Preparation

The procurement of suitable foods entailed considerable difficulty because they had to be purchased in the fall and early winter after the processing season had finished. Table IV-1 describes the materials finally obtained.

It would have been preferable to have used corn and peas which had been scarified and sulfited before being frozen (IQF). The use of unsulfited peas and the thawing, sulfiting, and refreezing of corn were less desirable procedures made necessary by the circumstances.

The peaches had apparently been picked before they were fully ripe since they shrank badly at every attempt to freeze dry them. Fruit thaws at a low temperature, perhaps below 0°F, due to its high content of dissolved sugars; and the fruit structure cannot be very permeable since the partial pressure of water vapor inside can build up quite readily to the point where thawing takes place. Because mature fruit freeze dries better than green fruit, the structure must become more permeable on ripening.

B. Preparation of Control Batches of Food by Vacuum Freeze Drying

For comparison with foods dried by the LPCS procedure, samples of the same materials were freeze dried in the conventional manner under very conservative (low temperature, low pressure) conditions. Table IV-2 describes the various vacuum drying runs.

The procedure for each of these runs was similar, with the frozen food being loaded on to trays in a cold room at about -5°F. Thermocouples were inserted into the samples while they were in the cold room. The trays were then transferred quickly to a freeze-drying chamber which was immediately sealed and evacuated. The time between removal from the cold room and reaching a pressure below 1 millimeter in the drying chamber was about 15 minutes. The chamber was always evacuated to about 100 microns before turning on the heat.

At the end of the drying time, the vacuum was broken with nitrogen, the chamber was opened, and the trays were quickly transferred to a dry room (relative humidity 10 to 30%) where the food was put into plastic bags.

The food was then loaded into No. 10 cans in the dry room, tops were loosely put in place, and the cans were evacuated twice with the vacuum being broken each time by nitrogen. and then they were sealed. The product was thus packed under nitrogen at atmospheric pressure.

C. Pilot Scale LPCS Apparatus

1. Figure IV-1 and Table IV-3 describe the apparatus. In the flow sheet, liquid heptane was sprayed onto steam heated tubes in the heptane boiler; the vapor then flowed over steam-heated, finned tubes in the superheater and through an orifice into the drying chamber. In the

TABLE IV-1

FOODS USED IN THE PREPARATION OF PILOT SCALE DRIED SAMPLES

Beef, Cooked - Commercial Cow - Canner and Cutter Grade Diced to approximately 3/8" and pressure cooked Pieces individually quick frozen (IQF)	Meat lean with occasional pieces of fat. Prepared by Bright Foods Company, Turlock, California.
Beef, Raw - Commercial Cow - Canner and Cutter Grade Diced to approximately 1/2" (IQF)	Prepared by Bright Foods Company, Turlock, California.
Chicken - Large Stewing Grade Cooked, boned, diced to approximately 3/8" (IQF)	Prepared by Bright Foods Company, Turlock, California
Fish - Ling Cod Filets Cut by hand to approximately 1/2" dices Frozen on trays at approximately 10°F	
Shrimp, Cooked Whole, peeled and deveined (IQF)	
Peas, Scarified Not sulfited, [illegible], then tempered and scarified	From California Vegetable Concentrates Company, Modesto, California

TABLE IV-1 (Cont'd)

Corn, Whole Kernel (IQF) Thawed, sulfited, and refrozen on trays in 1/2" layer at -5°F in freezer with forced air circulation.	Kernels stuck together loosely when refrozen. Sulfiting Procedure: Thawed at room temperature, soaked and stirred for one and a half minutes, then kernels recovered from solution on a screen, drained and refrozen. Sulfiting solution 300 ppm. 20 liters used for every 30 pounds of frozen corn. Analyses for absorbed SO_2 are described in Appendix III. Results were inconclusive.
Strawberries Sliced (IQF)	Obtained from producer of freeze-dried strawberries. No data available about processing. Only available source of suitable fruit.
Peaches, Rio Oso Gems Sliced, treated with light mixture of ascorbic acid and sulfite (IQF)	Prepared by Mantica Frozen Foods, Mantica, California.

TABLE IV-2

DRYING RUNS IN CONVENTIONAL FREEZE DRY CHAMBER WITH SAME FOODS USED IN LPCS PILOT-SCALE APPARATUS

Food	Run	No. Trays (21 x 36 in.)	Weight #, in/out	Temp. start/end °F.	Press Max; microns	Time hrs.
Beef, cooked	C-4	4	40.0/15.4	130°	170	19
	C-5	1	10.0/2.2	120°	200	25
Beef, raw	C-5	2	20.0/6.4	120°	200	25
	C-11	2	20.0/6.0	180° *	125	14
Chicken	C-6	4	32.0/12.2	135°		18
Fish-raw	C-8	3	30.0/6.0	120°	150 app.	
	C-11	1	10.0/2.0	180° *	125	14
Shrimp	C-8	1	10.0/.95	120°	150 app.	
Peas	C-1	2	20.0/4.0	180°/130°		21
	C-2	4	40.0/8.5	190°/130°	370	22
	C-5	1	10.0/1.8	120°	200	25
Corn	C-10	4	40.0/5.5	110°		16) 26 Total
				135°		10)
Strawberries	C-7	2	16.0/1.55	120°	140	
	C-9	1	5.4/.50	120°		
	C-12	4	38.7/3.9	120°		18
Peaches	C-9	3	30.0/3.0	120°		

* Temperature inadvertently kept at 180°.

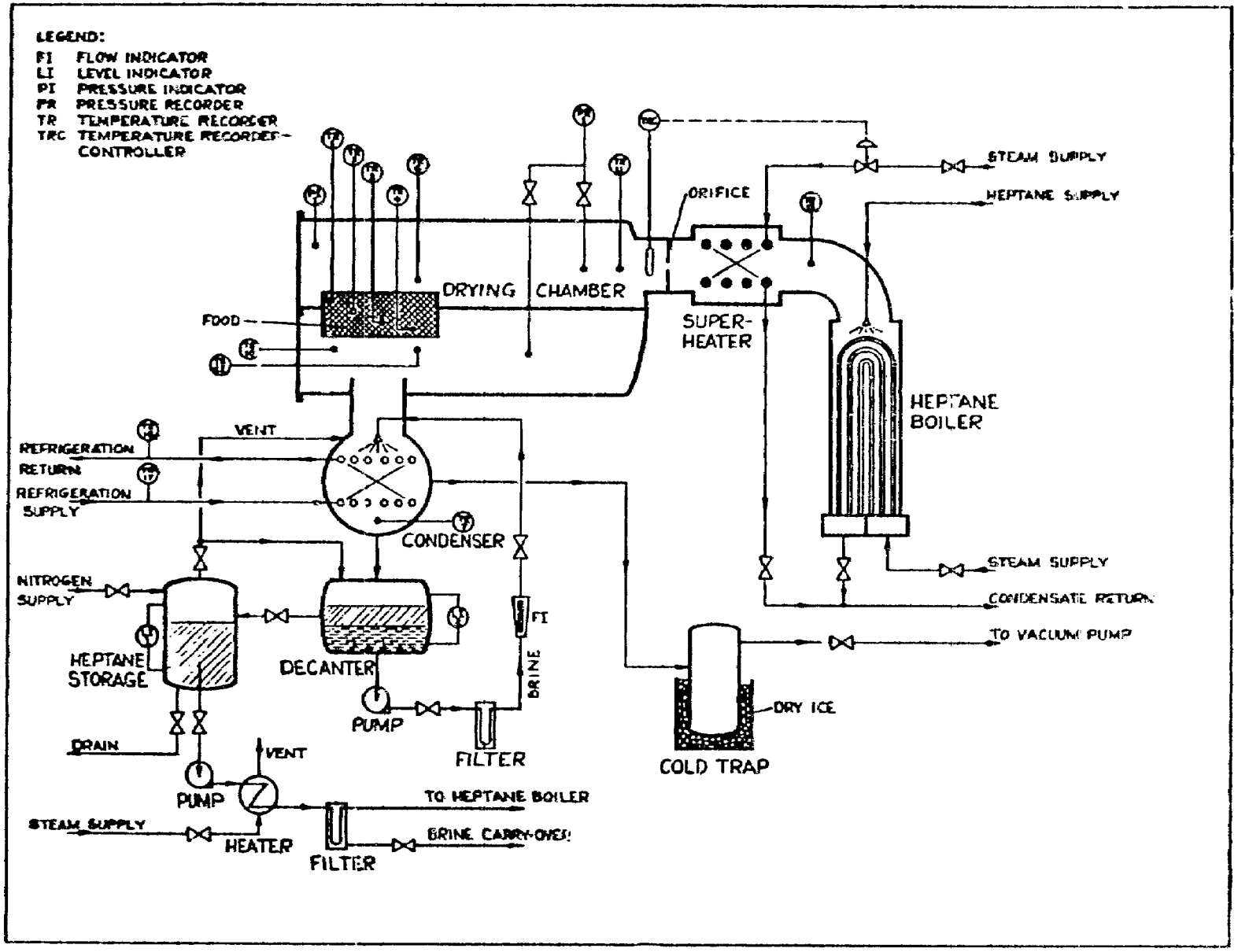


FIGURE IV-1 LOW PRESSURE CARRIER SUBLIMATION APPARATUS — PILOT SCALE

TABLE IV - 3

PILOT SCALE LPCS APPARATUS - DETAILS

Chamber	- Cylinder 36" diam. x 52" long
Superheater	- 6 tubes, each 23" long, 1 1/4" Sch. 40 pipe with fins 2" diam., spaced 1/4" apart.
Heptane boiler	- Shell 8" pipe Sch. 40, x 30" long. 32 each 5/8" O.D. hairpin tubes, each approx. 60" long. Heat transfer surface 21 sq.ft.
Condenser	- 78 each 5/8" O.D. hairpin tubes, each 76" to 80" long. Heat transfer surface approx. 80 sq.ft.
Food basket	- Drying bed 18 1/2" x 11 1/2", or 1.48 sq.ft.
Orifice	- 1" diam.
Heptane pump	- 1" gear pump, with 10 to 1 speed reducer and variable speed drive.
Brine circulating pump	- 1" Moyno, Type CDQ
Cold trap	- 14" diam., x 44" long
Decanter and heptane storage	- 16" diam. x 18" long
Vacuum pump	- 250 cfm displacement. Blank-off at 10 microns.
Heptane filter	- Fuel filter which passed hydrocarbons but not aqueous liquids.

drying chamber the vapor passed downward through the bed of food and into the condenser from which the liquid drained into the decanter. The liquid heptane floated off the top of the decanter into the heptane storage tank where it was pumped around the cycle again. From the pump the liquid was heated and then passed through a fuel filter which was readily permeable to the hydrocarbon but which held back droplets of water because of their higher surface tension, and in this way salt deposits on the boiler tubes were avoided. Between the filter and the boiler, and not shown on the flow sheet, was a flowmeter and a manual control valve by which the flow of heptane could be regulated.

A solution of brine, approximately 30% calcium chloride, was sprayed over the condenser tubes to prevent their being caked with ice. The decanter separated this brine from the liquid heptane, and the brine was continuously filtered and recirculated.

Because of the flammability of heptane, careful precautions were taken to avoid an explosion. The room containing the apparatus was well ventilated; explosion-proof motors, lights, and wiring were used in the vicinity of the apparatus; and an automatic system to purge the apparatus with nitrogen and to shut off the heptane flow in case of power failure or in case the vacuum was accidentally broken with air was used. Two pressure switches in series, which were each closed by vacuum, operated a solenoid valve (current to open) in the heptane supply line to the boiler and another solenoid valve (current to close) which would open when it was deenergized and purge the chamber with nitrogen. This same safety system is shown in Figure II-1 for the four-inch apparatus.

The purpose of the orifice between the superheater and the drying chamber was to have a somewhat higher pressure in the boiler in order to get better heat transfer between the hot surfaces and the vapor. In normal operation the pressure in the boiler was 5 to 10 psi absolute when using a 1" orifice and vaporizing about 1/2 gpm of liquid heptane. Without the orifice the vapor velocity was so high that droplets of liquid were carried out of the boiler and through the superheater into the drying chamber; and the elbow between the boiler and the superheater would be covered with frost on the outside from the low boiling liquid impinging on it from the inside. The 1" orifice solved this problem nicely and the surfaces of the boiler and superheater were quite warm except when the operation was badly upset.

2. To start a run, the vacuum pump was started, the cold trap was filled with dry ice, the refrigeration turned on, and the brine circulation was started. The food basket was loaded in the cold room and fine thermocouples (36 gauge) were inserted into food particles distributed about the bed. When everything was ready, the food basket was quickly transferred to the drying chamber, the thermocouple leads were connected with those in the chamber, and the chamber was evacuated to less than 1 millimeter, all within 5 minutes or less. The vent to the heptane storage tank was opened, which made the liquid boil until it cooled to its equilibrium temperature and then the flow of heptane was started. This sequence required about 5 minutes also. The flows of heptane and steam to the boiler were controlled manually and unless trouble developed, the apparatus operated very smoothly. Figures IV-2 and 3 show temperature

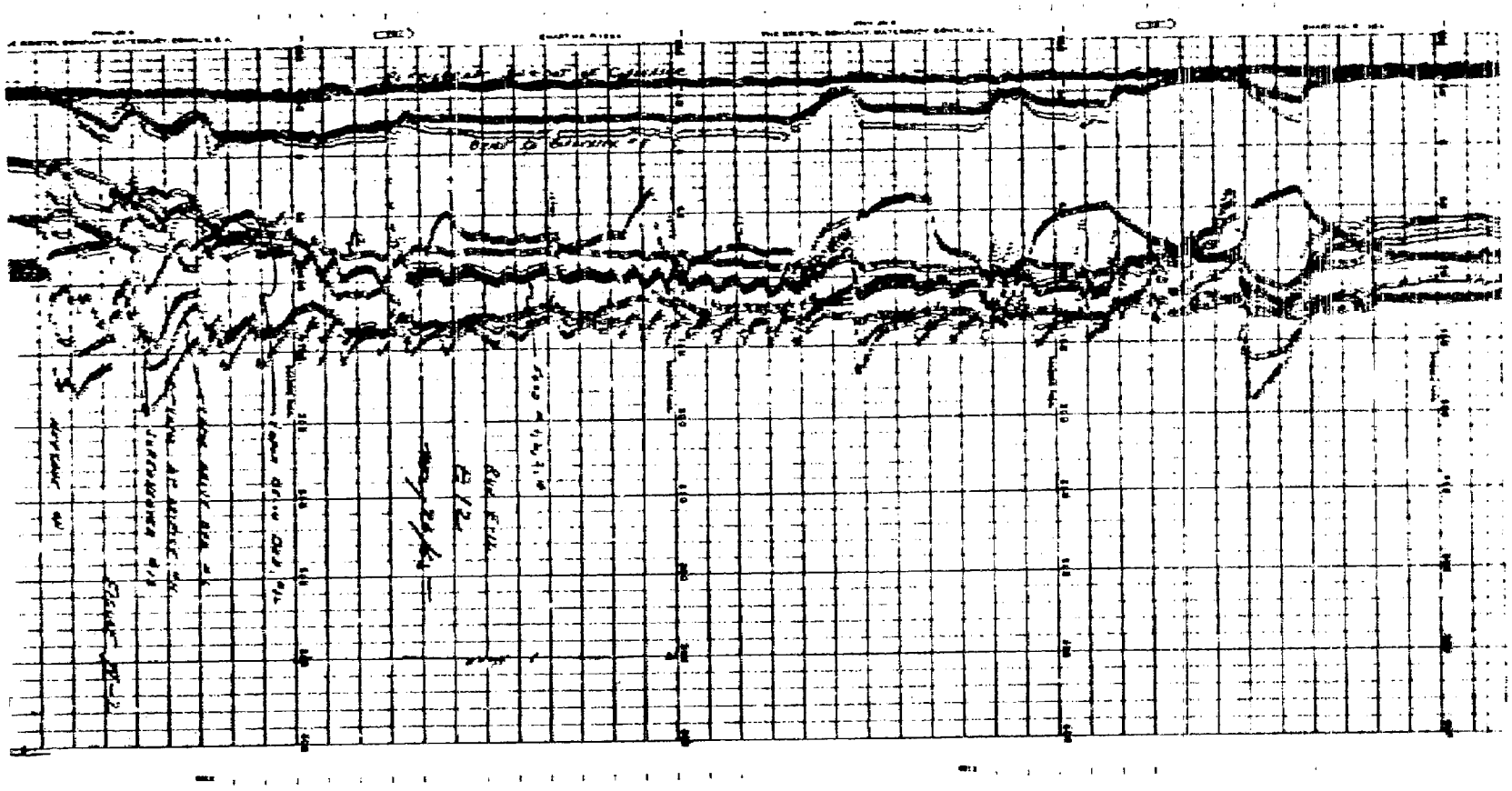


FIGURE IV-2 RUN E12 PEAS, SCARIFIED

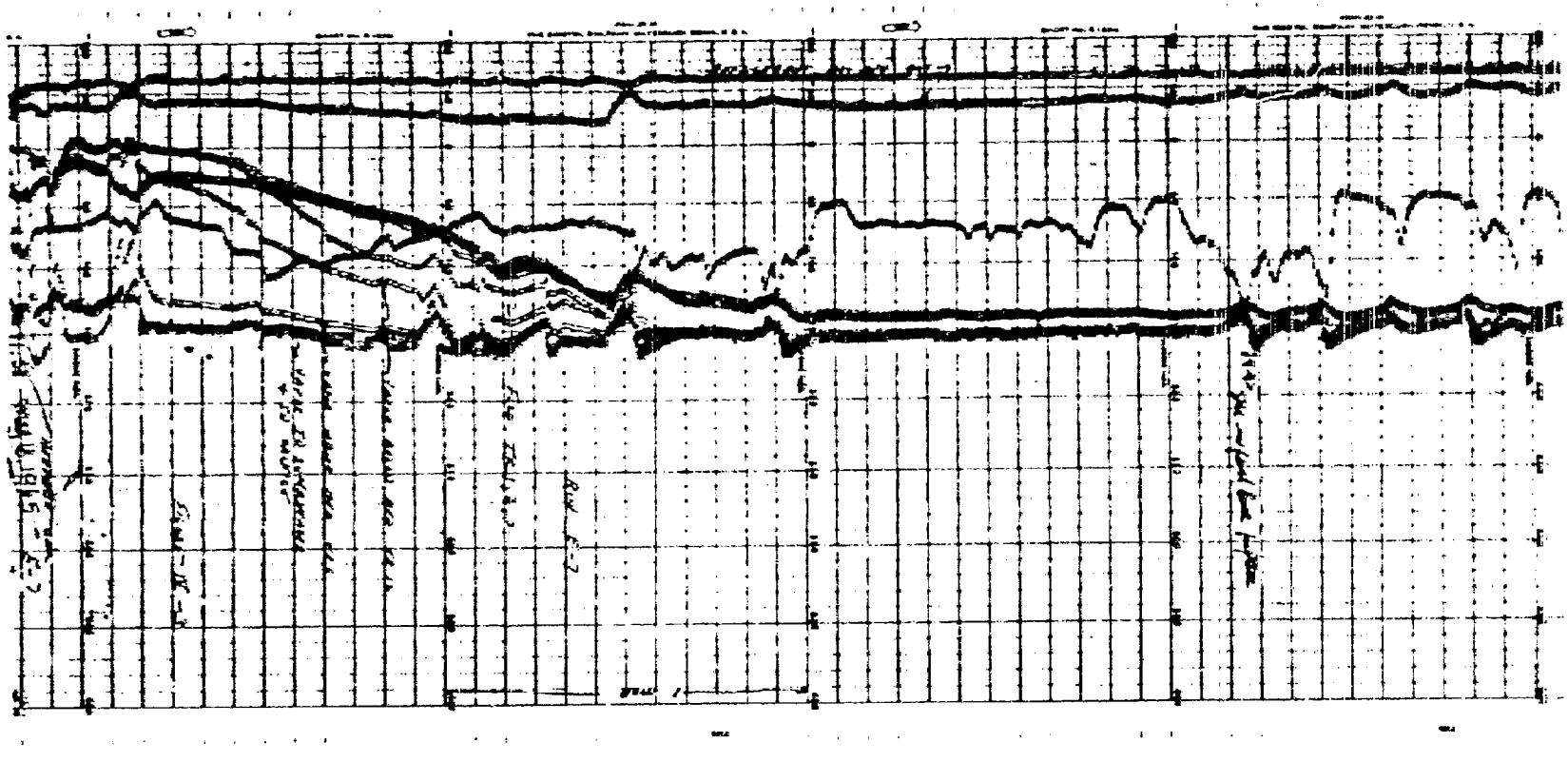


FIGURE IV-3 RUN E7 CHICKEN, COOKED AND DICED

recorder charts for two runs. In Figure IV-2, upsets were frequent whereas Figure IV-3 shows a comparatively smooth, trouble-free operation.

The temperature of the vapor leaving the bed is on the order of 50° in Run E-12, Figure IV-2, and this represents a drop of nearly 100° as the vapor passed through the bed. Naturally this temperature increased as the drying progressed.

The pressures used in the pilot scale drying (2.5 to 5.0 mm Hg) are rather low, but since the evacuation capacity and refrigeration were available to maintain these pressures, samples were produced under as favorable conditions as possible.

3. Table IV-4 summarizes the operation of the pilot scale LPCS apparatus and the conditions under which foods were dried. The dried foods were canned under nitrogen and sent to U. S. Army Natick Laboratories for detailed evaluation.

The original intention was to produce 10 pounds of each dried food, but the unanticipated problems in making the apparatus operational, and in operating it for extended periods, permitted preparation of only from 3/4 to 4 pounds of each sample.

In Table IV-4 difficulties or upsets in operation of the apparatus are noted. Probably the occurrence having most significance to the final product was in run E-4 where the orifice between the superheater and drying chamber blew out and incompletely vaporized carrier sprayed into the drying chamber briefly. The liquid heptane that wet the food momentarily evaporated very quickly, but a very strong after taste was apparent in the dried product.

4. The principal and rather unexpected problem which developed in operating the pilot scale apparatus was the formation of curdy suspended solids in the heptane layer of the decanter. As a run progressed, this material apparently clogged the line connecting the decanter with the heptane storage tank, and also the entrance of the heptane pump; the restriction caused the heptane pump to lose suction rather frequently. The heater shown in the heptane line just downstream from the pump in Figure IV-1 was installed to melt these curds, and they gave no trouble in the line beyond the heater. However, whenever the suction to the pump or the line between the decanter and storage tank clogged, they had to be purged by putting some nitrogen pressure into the storage tank and blowing the solids through. Toward the later part of a run, this purging had to be done every 10 or 15 minutes; and even though the operation required no more than 2 or 3 minutes, it upset the drying conditions.

This solid material which built up gradually and had about the same density as heptane, is believed to be a hydrate of heptane. The fact that the water drained from the fuel filter in the heptane line at the end of a run generally contained much less salt than the calcium chloride brine circulated through the condenser, is evidence that the filter collected very little entrained brine and that the water on it came from the thermal decomposition of a solid compound formed between the heptane

TABLE IV - 4

DRYING RUNS ON LPCS PILOT-SCALE APPARATUS

Food	Run	Temp. °F.	Press mm Hg	Time hrs.	Loading #/ft.	Carrier Flow #/(ft²-min.)	Weight in/out #	Remarks
Beef-cooked	E-4	130-150	2.5-4.0	5.5	2.0	2.4	3.0/1.2	Control erratic.
		Some Heptane sprayed onto product.						
Beef-raw	E-5	130	2.5-4.0	3.5	3.4	2.7	5.0/1.35	
	E-6	150-160	2.0-5.0	7.4	6.9	3.4	10.0/3.05	After run, product
		held in unit 2-1/2 days below 2 mm Hg, then canned.						
Chicken-cooked	E-7	150	3.5	4.5	3.4	2.4	5.0/1.7	Very smooth operation.
		Effective drying time - 2.5 hours.						
Fish-raw	E-3	110-150	2.0-3.5	5.5	3.4	2.7-3.4	5.0/1.25	Trouble w/temp.
		control - vapor up to 200° several times.						
Shrimp	E-10	140	2.0-4.0	4.5	3.4	2.7	5.0/.7	Finished in
		vacuum chamber, overnight at 50 microns.						
Peas	E-2	140-150	3.0	3.0	2.1	1.1-4.4	3.0/.55	Temps cycled badly.
	E-12	130-140	1.5-3.5	3.0	3.4	2.7	5.0/.8	Finished in
		vacuum chamber, overnight at 50 microns.						
Corn	E-14	130	2.0-3.0	5.5	3.4	2.3-3.4	5.0/.9	Operation very
		smooth. Reagent Heptane used w/out sulfuric acid treatment.						
Strawberries	E-9	110-150	2.5-3.5	5.0	3.4	2.7	5.0/.45	Much trouble
		with carrier flow. Very little shrinkage.						
	E-11	140	2.5-3.5	4.5	3.4	2.7	5.0/.4	Considerable
		shrinkage.						
Peaches	E-13	110-120	2.0-3.0	6.0	3.4	3.4	5.0/.35	Operation smooth.
		Product very badly shrunken. Reagent Heptane used w/out sulfuric acid treatment.						

and water. The formation of solid or jelly-like hydrates from lower hydrocarbons and water and from alkyl halides and water is well known; and the phenomenon is used to obtain fresh water from salt water. At the high pressures in natural gas pipe lines traces of water will cause jelly-like hydrates to deposit at temperatures several degrees above the normal freezing point of water.

These solids accumulated slowly in the heptane decanting and storage tanks, and the only difficulty they caused was the clogging at constricted points in the system. They were never apparent after the liquid was warmed, but heating was not possible until the heptane had passed through the circulating pump.

When the suction to the heptane pump was partly clogged, there was a tendency for the pump to cavitate and to lose suction. Cavitation took place rather readily because of the low pressure under which the pump suction operated, but this problem was largely eliminated by locating the pump approximately 3 feet below the heptane storage tank and providing 3 or 4 feet of liquid head and a straight run of 1" pipe to carry liquid to the pumps.

Vaporization of the heptane proved to be somewhat difficult in the boiler which Figure IV-1 shows. When liquid was sprayed on to the hot tubes in the boiler at less than 10 millimeters of pressure, the large volume of vapor and the resulting high vapor velocities carried droplets of liquid through the superheater over into the drying chamber, but installation of the orifice, which raised the pressure in the boiler to half an atmosphere or higher, lowered the vapor velocities and eliminated this carry-over difficulty.

Even with the orifice installed, the carrier temperature oscillated 10° or more because heat transfer to the bulb operating the temperature controller was slow, and the superheater stored enough steam and sensible heat so that after the controller acted there was some lag before the temperature of the carrier vapor decreased. The best control was obtained when the temperature controller acted on an on-off basis, essentially.

Corrosion would have been a problem in the condenser if the equipment had operated for any prolonged period. The condenser tubes were copper, the shell of the condenser was mild steel, and in contact with the concentrated calcium chloride brine, there was evidence of corrosion. No problems or significant damage were caused by corrosion in the operations reported here, however.

V. CONDENSIBLE CARRIER FLUIDS

A. Comparison of Properties

The obvious attributes for carrier fluids to be used in this process where the vapor is circulated by evaporation and condensation are, first, that the material be non-toxic and inert, and second that it have the right volatility:

too high a vapor pressure would necessitate excessively low condenser temperatures while too low a vapor pressure would cause the carrier to condense on the frozen food at 3 to 15 mm Hg.

Three fluids which appear to have the desired properties were studied: heptane, with which most of the work was done, hexane, and FC-75, a cyclic fluoro-ether $C_8F_{16}O$. Their pertinent properties are tabulated in Table V-1.

Since the minimum flow of carrier vapor is probably determined by its ability to carry heat to the bed of food (for very thin beds carrying water away may determine the limiting rate) while heat removed by the refrigerated condenser determines the cost of circulating the carrier fluid, a desirable characteristic would be a low ratio of ΔH of vaporization to the heat capacity of the fluid. Table V-1 gives the ratio of the change in enthalpy in the condenser to the heat capacity, and FC-75 is decidedly lower than either of the hydrocarbons. Thus with FC-75, a given amount of heat can be transferred to a bed of drying food with much less refrigeration than is the case for heptane or hexane, and also less heat would be required to vaporize this carrier.

Regarding volatility, FC-75 and heptane are quite similar and would allow reasonable condenser and ice core temperatures for operating pressures between about 3 and 7 or 8 mm Hg. Hexane is somewhat more volatile, and either higher operating pressure or a lower condenser temperature would be needed.

Since the thermal conductivity of the vapor helps determine the rate of heat transfer through the porous dried shell of the food, the highest value of this property would be desirable. Here heptane is superior to FC-75.

The diffusivity of water vapor in the carrier gas determines the partial pressure of water at the ice core, and thus the ice core temperature for a given rate of heat transfer. The inert carrier interferes with the flow of water vapor out from the ice core, and in fact causes the mass transfer to take place by diffusion.

The diffusivity of water vapor would, however, be only slightly less in FC-75 than it would be in heptane or hexane, since the molecular weight of the heavier gas has very little effect, as can be seen by the expression for the diffusivity for the counter diffusion of two ideal gasses (10):

$$D \sim \frac{1}{P}\left[T^3\left(\frac{1}{M_a} + \frac{1}{M_b}\right)\right]^{1/2}$$

Flammability of the hydrocarbons is a disadvantage to their use, although the hazard can be controlled. As the pressure of a system is decreased, the upper and lower explosion limits for a combustible vapor tend to draw together, and there is a minimum pressure of approximately 5 to 10 millimeters below which the gas cannot be ignited in air (11). Thus within the drying chamber there is little or no fire hazard unless the vacuum is broken by air. FC-75 is, of course, non-flammable. Generally a chlorinated or fluorinated solvent with hydrocarbon dissolved in it is non-flammable if the concentration of hydrocarbon is below 20% by weight.

TABLE V - 1

COMPARISON OF CARRIER PROPERTIES (12, 8)

	FC-75	n-HEPTANE	n-HEXANE
Heat Capacity of Vapor @ 150° F BTU/# ° F	.23	.435	.435
ΔH from Liquid at 0° F to Vapor @ 150° F, BTU/#	49.7	210	210
ΔH/(Heat Capacity)	217	483	483
Vapor Pressure, mm Hg			
20° F	8.0	7.8	33
-10° F	2.8	2.4	4.5
Thermal Conductivity, Vapor @ 210° F, BTU/(hr. °F ft.)	.008	.012	.013
Molecular weight	416	100	86

With regard to toxicity, neither the FC-75 nor the saturated hydrocarbons is known to be harmful. The Food and Drug Administration allows 30 ppm of hydrocarbon oil (an alliphatic kerosene fraction) as residue from its use as a defoaming agent in the manufacture of beet sugar, and 25 ppm of hexane is allowed as a residual solvent in flavor extracts. No tolerance has been set for FC-75, but completely fluorinated organic compounds are extremely inert and non-toxic and a somewhat similar material, Freon C318, a cyclic saturated fluro carbon C_4F_8 has been cleared by the Food and Drug Administration for use as a propellant of foodstuffs, presumably whipped cream. Thus any of these solvents should be satisfactorily safe to use.

The possibility exists of using mixtures of carrier fluids, and since the carrier is completely vaporized and completely condensed in the cycle, no fractionation should occur. However, a close boiling mixture would be desirable because the pressure at which condensation would occur on the ice core corresponds to the dew point of a mixture, and the temperature at which condensation would be complete, or virtually so, would be the bubble point of the mixture; so the minimum allowable volatility would be determined by the heaviest component and the maximum by the lightest. Certainly, however, a close boiling mixture of saturated hydrocarbon isomers should be satisfactory.

The cost of the carrier fluid is a highly practical matter, and here the hydrocarbons are heavy favorites. FC-75 costs about $1 per pound compared to about 20¢ a pound for the purified hydrocarbons. However, since the density of FC-75 (1.77 compared to .68) is much higher than that for the hydrocarbons, about twice the weight of it would be needed; and therefore its cost is about 10 times as great. Therefore, despite the more favorable theoretical arguments for FC-75, its greater cost and lack of a Food and Drug Administration tolerance would probably make heptane the most expedient fluid to use on a large scale; and thus most of this work has been done with heptane.

B. Performance of Different Carrier Fluids

Table V-2 lists the drying runs made in the small scale apparatus with hexane and with FC-75. Table II-1 gives similar data for heptane. All three carrier fluids seem to perform quite well, although the condenser in the apparatus was not adequate to handle the higher flow rates of hexane at 8 millimeters, the lowest pressure used with this carrier.

C. Residues of Carrier Fluid in the Dried Foods

In all of the small-scale work reported in Table II-1, reagent grade heptane was used; but this material was not readily available in the quantities needed for the pilot scale apparatus so that two barrels of technical grade heptane (Amsco) were ordered for the larger scale work.

In the small scale runs, at the most only a faint after taste, which might be attributed to the heptane was noticed in some of the dried samples; but the first samples dried in the pilot scale apparatus had a strong acrid taste and had obviously been contaminated by the carrier.

TABLE V - 2

USE OF CARRIER FLUIDS OTHER THAN HEPTANE

Run No.	MOISTURE % Before	After	TIME min.	TEMP. °F	PRESS. mm Hg	LOADING #/ft.^{2}	FLOW #/ft.^{2}-min.	RETENTION gm/100 gm.	TIME STORED Days	RESULTS
					A. HEXANE					
1) COOKED BEEF DRIED IN WT.-TIME APPARATUS, 3 gm./run, 3/8" dices.										
144	74 (app)		82	150	8			95	8	Flavor fair. Possible after-taste.
142			105	150	15			81	9	Good flavor. Tough.
147			102	150	20			64	6	Good flavor. Possible after-taste
146			115	150	30			80	7	Fair flavor. Possible after-taste
143			92	150	50			68	8	Good flavor.
2) SLICED STRAWBERRIES, DRIED IN 2 IN. BED.										
150	90 (app)	6.4	250	130	8	5.6	.82	256	1	Somewhat shrunken. Good flavor & color.
149		5.8		130	8	5.9	.82	206	1	Somewhat shrunken. Good flavor & color.
148		4.7	300	130	15	6.0	.82	197	5	Badly shrunken. Good flavor & color.

Run No.	MOISTURE % Before	After	TIME min.	TEMP. °F	PRESS. mm Hg	LOADING #/ft.^{2}	FLOW #/ft.^{2}-min.	RETENTION gm/100 gm.	TIME STORED Days	RESULTS
					B.	FC - 75, $C_8F_{16}O$				
1) COOKED BEEF, DRIED IN 2 IN. BED., 3/8 in dices.										
151	74 (app)	1.2	320	150	6	6.5	2.7	103	71	Fair flavor. Slight after-taste.
152			180	150	6	5.0	2.7			
2) FISH - approx. 3/8 IN. DICES.										
153		1.3	240	150	6	5.8	6.7	189	65	Good flavor. No apparent shrinkage.
3) STRAWBERRIES - SLICED										
154	90 (app)	1.0	325	130	3.5	5.6	4.0	254	65	Slight shrinkage. Good flavor.
155			390	130	2.5	5.6	2.7			Sample not dry, frozen inside No thawing.

Table V - 2 (Cont'd)

The technical grade heptane turned out to be quite different from the analytical grade. The ultraviolet spectrum for the analytical material showed no less than 90% transmittance from the visible to the far ultraviolet (350 to 200 millimicrons) while the transmittance of the technical grade fell to virtually 0 between 300 and 280 millimicrons. Furthermore, the chromatograph showed the technical grade to contain at least 4 and possibly 5 princip ' components while the other had only 1 major component. See Figure V-1.

Since paraffin hydrocarbons are transparent in the ultraviolet, the high absorbance of the technical grade heptane was undoubtedly due to aromatic and possibly also to unsaturated impurities. These materials, being more reactive than the saturated hydrocarbons, can be removed by treatment with fuming sulphuric acid and also, but less readily, by adsorption on activated carbon and by treatment with concentrated sulphuric acid. Thoroughly washing the technical grade heptane twice with about 25% by volume of fuming sulphuric acid, (20% sulfur trioxide) and at the same time warming to about 150°F, then decanting and washing the hydrocarbon with water, made it quite transparent through this full range of the ultraviolet and apparently thoroughly removed the aromatics. Treating the technical grade heptane with active carbon and with concentrated sulphuric acid decreased its absorbance in the ultraviolet to some extent but not nearly so dramatically as did the fuming sulphuric acid.

The technical grade heptane used in the pilot apparatus for runs E-2 through E-12 was treated with fuming sulphuric acid in the manner described above, but apparently in the 3 to 5 gallon batches contact between the acid and hydrocarbon was insufficient and significant quantities of aromatic materials remained in the carrier fluid as indicated by UV spectra and by analysis of the food for residual carrier.

Samples of dried food were analyzed for residues of carrier using a mass spectrograph. Weighed samples of the foods were sealed into glass ampoules which were then broken under vacuum in the chamber of the mass spectrograph and the volatile materials determined from the spectrum. The results are reported in Table V-3. Where the foods were dried in the small scale apparatus with analytical grade heptane and hexane and with FC-75, no compounds other than the carrier were detected and only for Run 154 was an excessive quantity of carrier found. In Run 154 the pressure was only 3.5 millimeters compared to 8 and 15 in Runs 149 and 148, so the ice core temperature of the strawberries in this run should have been much lower than in the others. Perhaps this fact accounted for the high residual content of FC-75 in this case.

The E series of runs, which were made in the pilot scale apparatus using the technical grade heptane (purification had been attempted) showed considerable aromatic residues of toluene and alkyl benzenes in addition to saturated C_7s, heptane, and methyl cyclohexane. The comparitively large residues of toluene indicate that it is adsorbed preferentially by the dried food, and this is logical considering that it is a considerably more powerful solvent than the saturated hydrocarbons. Adsorbed aromatics probably contribute most to aftertaste, since heptane itself should be tasteless.

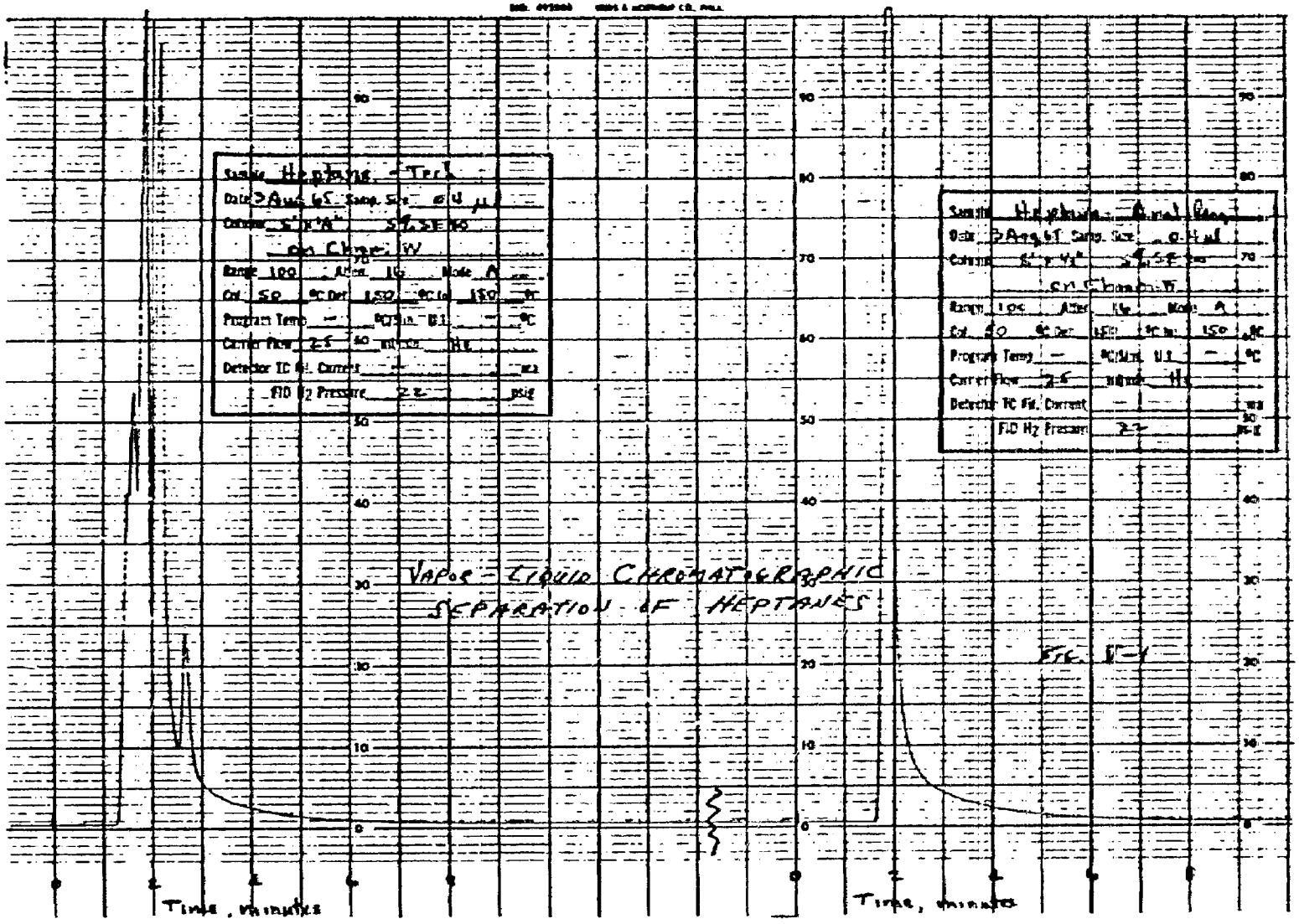


FIGURE V-1 VAPOR-LIQUID CHROMATOGRAPHIC SEPARATION OF HEPTANES

TABLE V - 3

RESIDUES OF CARRIER IN DRIED FOODS

Run No.	FOOD	CARRIER	RESIDUE, ppm
137	Beef, cooked	Heptane- AR	Heptane, 27
138	" "	" "	Heptane, 20
148	Strawberry	Hexane, AR	Hexane, 12
149	"	" "	Hexane, 7
151	Beef, cooked	FC - 75	None detected
153	Fish	FC - 75	None detected
154	Strawberry	FC - 75	100 (approx.)

			HEPTANE	METHYL CYCLO-HEXANE	TOLUENE	ALKYL BENZENES
E- 2	Peas	Heptane-Tech	17	10	50	None
E-12	Peas	"	6	2.5	1.1	1.3
E- 4	Beef, cooked	"	90	58	100	6
E- 6	Beef, raw	"	None	2.2	6	5
E- 5	Beef, raw	"	6	2.4	10	None
E- 7	Chicken, cooked	"	7	2	16	4.7
E- 3	Fish	"	10	2.5	8	6.5
E- 8	Peaches*	"	470	200	55	11

*(Dried sample E-8 had a strong acrid taste, and was discarded.)

In Run E-4 the orifice ahead of the drying chamber blew out, and droplets of liquid carrier were blown on to the food during part of the run. No liquid carrier was known to have passed into the drying chamber in Run E-8, but this must have happened; and since the product had a very strong unpleasant taste, it was discarded.

As pointed out above, the Food and Drug Administration allows 25 ppm of hexane as residual solvent in spice flavor extracts and 30 parts per million of aliphatic hydrocarbon oils of a kerosene fraction in beet sugar (11.): the content of carrier fluid shown in Table V-3 for Runs 137 through 153 where properly purified material was used should be satisfactory from the point of view of residues. There appears to be no reason, however, why technical grade heptane cannot be used if the aromatics are satisfactorily removed. Fuming sulphuric acid will effectively separate these aromatic impurities from saturated hydrocarbons, and the design of an apparatus to do this should present no problems for the comparatively small amounts of heptane needed to supply a full-scale version of this process.

VI. PROCESS DESIGN CONSIDERATIONS

While developing details of design was not an objective of this work, a certain amount of this information did come out of the effort and the principal points are briefly noted below.

Countercurrent flow between the carrier vapor and the food is essential in a continuous process so that the carrier fluid can transport the maximum possible amount of moisture from the bed by contacting undried food just before it leaves.

Since the flow of carrier fluid is most likely to be determined by the amount of available sensible heat it can carry to the bed, supplemental heating of the vapor at an intermediate stage of contact is likely to minimize the carrier flow necessary.

For a situation where the carrier vapor flows through a bed of food, increased bed depth (as on a moving grate) increases the over-all drying time needed, but it decreases the cost per unit of drying time. Thus, for a given material and a given flow of carrier, there should be an optimum bed depth.

Traces of aromatic and unsaturated compounds and also oxygenated compounds can be removed from saturated heptane by scrubbing with warm, fuming sulphuric acid. Since traces of these impurities impart undesirable taste and odor to the food, any process designed should incorporate apparatus for cleaning up the carrier.

To minimize loss of carrier fluid, leaks in the vacuum system should be minimized. Any inert gas removed by the vacuum pump carries with it a certain amount of carrier vapor and provision should be made to control the chamber pressure by throttling the vacuum pump.

Carrier liquid can be vaporized and superheated most efficiently by flash vaporization in a tube heater at a pressure such that the temperature of the saturated vapor is only slightly above the desired vapor temperature in the drying chamber. Then by throttling the saturated vapor down to the desired chamber pressure, it can be superheated without having to contend with the low heat transfer coefficient of gas films at low pressure.

The condensing, decanting, and liquid carrier system should provide for solid hydrates. These form at low temperature in the condenser and can be decomposed by pumping them up to atmospheric pressure, warming to room temperature and then filtering out the water.

APPENDIX I

BIBLIOGRAPHY

1) Report # R-1910, The LPCS Freeze-Dry System. FMC Corp., Central Engr. Labs, Pg. 7.

2) Harper, Unpublished communication (1963)

3) Barth, et al, Process for Low Pressure Carrier Sublimation, U. S. Patent Application SN 271,083.

4) Ginnette, et al, Freeze Drying Rates. 1958, Fifth National Symposium on Vacuum Technology, Trans., Pg. 268.

5) Harper and Sahrigi, Thermal Conductivities of Gas-filled Porous Solids. I & E C Fundamentals, 3, #4, 318 (Nov. 1964).

6) Foust et al, Principles of Unit Operations, Wiley, NY (1960), Pg. 183.

7) Proposal for Study of Carrier Gas Freeze-Drying at Low Pressure. #P-2027. Prepared for U.S. Army Natick Labs by FMC Corp., (Apr. 1964).

8) Maxwell, J. B., Data Book on Hydrocarbons, Van Nostrand, Pgs. 32, 89, 104.

9) Ref. 1) Figure 6.

10) Ref. 6) Pg. 106.

11) Limits of Flammability of Gases and Vapors. U. S. Bureau of Mines Bulletin 503, Pg. 3.

12) Technical Information, Minnesota Mining and Manufacturing Co. (Jan. 1962), 3M Brand Inert Fluorochemical Liquids.

13) Ref. 6, Pg. 120.

14) U. S. Dept.of Health, Education & Welfare, F.D. A., Compilation of Regulations for Food Additives, sub-part A, Pg. 11.1.

APPENDIX II

DEFINITION OF TERMS

P	Total pressure
p	Partial pressure of water vapor as variable, or at the ice core.
p_o	Partial pressure of water vapor at surface of particle
p_p	Partial pressure of water vapor in vapor stream
T	Temperature of ice core
T_o	Temperature of surface of particle
T_p	Temperature of vapor stream
T_{av}	Average temperature of dried food shell
y	Fraction of water vapor remaining in food
h	Film coefficient for heat transfer through boundary layer
k'_c	Mass transfer coefficient through boundary layer
k	Thermal conductivity of dried food
D	Diffusivity of water vapor through pores of dried food, against carrier vapor
ΔH	Change in enthalpy of water from ice to vapor
$\Delta\rho$	Change in density of food as it dries (assuming no shrinkage)
M	Molecular weight of water
Mc	Molecular weight of carrier fluid
r	Radius of ice core
r_o	Radius of particle
θ	Time

Definition of Terms (cont'd)

q	Rate of heat transfer
N	Rate of mass transfer
A	Cross-sectional area
C_p	Heat capacity of carrier vapor
G	Mass velocity - mass/(area-time) of carrier
k'	Thermal conductivity of carrier vapor
μ	Fluid viscosity

APPENDIX II

HEAT AND MASS TRANSFER CALCULATIONS

A. Heat transfer from stream of carrier vapor to the ice core of a spherical food particle. (4)

Heat transfer through boundary layer

$$q = h\left(4\pi r_o^2\right)\left(T_p - T_c\right) \qquad ; \text{ Assume } q +$$

Heat absorbed by the evaporating ice core

$$q = -\Delta H \Delta\rho \left(4/3\ \pi r_o^3\right) \frac{dy}{d\theta} \qquad ; \frac{dy}{d\theta} \text{ is } -$$

Equating expressions and rearranging

$$T_p - T_o = \frac{-\Delta H \Delta\rho\, r_o}{3h} \frac{dy}{d\theta}$$

Within the dried shell of the food particle

$$q = k\left(4\pi r^2\right) \frac{dT}{dr} \qquad ; \frac{dT}{dr} \text{ is } +$$

Solve for dT and integrate; at $r = r_o$, $T = T_o$

$$T_o - T = \frac{+q}{4\pi k}\left(\frac{1}{r} - \frac{1}{r_o}\right)$$

Above integration assumes q constant with r at any instant, i.e., heat capacity of the dried shell of food is negligible.

$$4/3\ \pi r^3 = 4/3\ \pi r_o y$$

and so,

$$r = r_o y^{1/3}$$

Substituting:

$$T_o - T = \frac{-\Delta H \Delta \rho r_o^2}{3k}\left[\frac{1}{y^{1/3}} - 1\right]\frac{dy}{d\theta}$$

Adding expressions for $T_p - T_o$ and $T_o - T$ gives

$$T_p - T = \frac{\Delta H \Delta \rho r_o}{3}\left[\frac{1}{h} + \frac{r_o}{k}\left(\frac{1}{y^{1/3}} - 1\right)\right]\frac{dy}{d\theta}$$

In the weight-time runs, T_p is constant, with θ and y, and variation of T is small, so that $(T_p - T)$ is approximately constant. Therefore, since $y = 1$ when $\theta = 0$, the above expression can be integrated to give:

(at $\theta = 0$, $y = 1$)

$$\theta = \frac{\Delta H \Delta \rho r_o}{3(T_p - T)}\left[\left(\frac{r_o}{2k} + \frac{1}{h}\right) + \left(\frac{r_o}{k} - \frac{1}{h}\right)y - \frac{3}{2}\frac{r_o}{k}y^{2/3}\right]$$

If a value for the ratio of $h/(k/r_o)$ is assumed, then the function of y in brackets can be evaluated, and it is proportional to θ. By evaluating a constant of proportionality at one experimental point, values of θ for other values of y can be calculated.

Rearranging the expression for $T_p - T$ gives

$$\frac{dy}{d\theta} = \frac{3(T_p - T)}{-\Delta H \Delta \rho r_o}\,\frac{1}{\left[\frac{1}{h} + \frac{r_o}{k}\left(\frac{1}{y^{1/3}} - 1\right)\right]}$$

B. Diffusion of Water Vapor out of a Spherical Food Particle (13)

For diffusion of gas a through gas b, the flux is:

$$(Na/A)t = -D\,(C_t/C_b)\,dCa/dX$$

Here $dX = -dr$

C_t = (moles/vol) total = P/RT for ideal gas

$C_b = (P - p)/RT$

$dCa = (1/RT)\,dp$

Na = moles water/time = $4/3\,\pi r_o^3 \left(\frac{\rho}{M}\right)\frac{dy}{d\theta}$

$A = 4\pi r^2$

$$\frac{Na}{4\pi r^2} = -D\,\frac{P}{P-p}\,\frac{1}{RT}\,\frac{dp}{dr}$$; Na is +, dp/dr is -

Assuming Na is constant with r at a given instant

$$\frac{dp}{P-p} = \frac{NaRT}{4\pi DP}\,\frac{dr}{r^2}$$

Where $r = r_o$, $p = p_o$, integrating, and assuming absolute value of T does not vary greatly with r, so that average value can be used:

$$\ln\left(\frac{P-p_o}{P-p}\right) = \frac{Na\,R\,T_{av}}{4\pi D P}\left(\frac{1}{r} - \frac{1}{r_o}\right)$$

And <u>if</u> P is much larger than p and p_o

$$\ln\left(\frac{P-p_o}{P-p}\right)$$ is approx. $\frac{P-p_o}{P-p} - 1 = \frac{p-p_o}{P-p}$

so that

$$p - p_o = \frac{P - p}{P} \frac{N_a RT}{4\pi D}\left(\frac{1}{r} - \frac{1}{r_o}\right)$$

For transfer of water vapor through boundary layer

$$N_a/A = k_c' (C_a - \bar{C}_a) = k_c'/RT (p_o - p_f)$$

and $$p_o - p_f = \frac{N_a R T_o}{4\pi r_o k_c'}$$

Adding $p_o - p_f$ to $p - p_o$ and substituting for r and Na gives

$$p - p_f = \frac{R \Delta\rho r_o}{3M}\left[\frac{T_o}{k_c'} + \frac{T_{av} r_o}{D}\left(\frac{1}{y^{1/3}} - 1\right)\right]\frac{dy}{d\theta}$$

$$\frac{dy}{d\theta} = \frac{3M(p - p_f)}{R \Delta\rho r_o} \frac{1}{\left[\frac{T_o}{k_c'} + \frac{T_{av} r_o}{D}\left(\frac{1}{y^{1/3}} - 1\right)\right]}$$

C. Variation of ice core temperature as drying proceeds

Equating above expressions for $dy/d\theta$ and rearranging, gives

$$\frac{T_f - T}{\rho - \rho_f} = \frac{a H M}{R T_\infty} \cdot \frac{\left[\frac{1}{k} + \frac{r_0}{k}\left(\frac{1}{y^{1/3}} - 1\right)\right]}{\left[\frac{1}{k_c'} + \frac{r_0}{D}\left(\frac{1}{y^{1/3}} - 1\right)\right]}$$

T_f and ρ_f are constant with y, and so are T and p if

$$\frac{h}{k/r_0} = \frac{k_c' T_\infty}{(D/r_0) T_0}$$

Since this is probably not true, the temperature of the ice core should vary somewhat as drying proceeds. Since y decreases, $(T_f - T)/(p - p_f)$ should decrease, and this would be caused by an increase in T.

D. Heat Transfer Film Coefficient around a Spherical Food Particle

From Foust (6) the factor j_q for transfer of heat between single spheres and a gas stream is plotted as a function of the Reynolds number based on gas mass flow rate and particle diameter, do = 1/4 inch.

$$j_q = \left(\frac{h}{C_p G}\right)\left(\frac{C_p \mu}{k'}\right)^{2/3}$$

For Heptane vapor at 150°f

C_p = .44 BTU/# - °F

μ = 6.5×10^{-3} C_p.

k' = 10^{-2} BTU/hr.-ft - °f

and, since Heptane is nearly an ideal gas at the pressures used here, these values are independent of pressure.

$C_p \mu / k'$ = .69 in consistent units

The mass velocity, G, for flow of vapor from 11 cc/min. of liquid Heptane through a channel 1 1/2 in. diam. is

$$\left(\frac{11\ (.68)}{60}\ \frac{\text{gms}}{\text{sec}}\right)\left(\frac{1}{454}\ \#/\text{gm}\right)\ \frac{144}{(3/2)^2\ (\pi/4)\ \text{ft.}^2}$$

= .0223 #/ft.^{2} - sec. = 80 #/hr.- ft^2

Reynolds no. = $\frac{d_o G}{\mu}$ = 106

From plot, j_q = .07

And h comes out 3.2 BTU/hr - °F - ft^2

To determine the influence of mass flow rate of carrier on h, the plot in Foust (6) shows that j_q is proportional to Reynolds No. to -.3 power.

Therefore $h \sim G(G^{-.3}) \sim G^{.7}$

Furthermore, h should not be affected by pressure, since C_p, μ and k, and G are each pressure-independent.

APPENDIX III

ANALYSIS FOR FREE SULFUR DIOXIDE IN CORN AFTER FREEZE-DRYING BY LPCS METHOD CE 9966

Purpose
To determine the amount of free SO_2 remaining on corn that was dipped into a 300 parts per million solution of SO_2 and freeze-dried by the LPCS method.

Materials
Frozen corn, "Libby's" Golden Sweet Whole Kernal Corn. A 300 ppm SO_2 solution made from Na_2SO_3.

Procedure
The 300 ppm SO_2 solution was made and checked by using the AOAC method. (AOAC para. 27.079, 9th Ed., 1960) The frozen corn was thawed, then soaked in the 300 ppm SO_2 solution for 1-1/2 minutes. The excess solution was removed by shaking. The corn was placed on freeze-drying trays 2 - 3 kernels deep and frozen to -10° F. in the cold room. The frozen material was then dried using the LPCS method. The dried corn was analyzed by using the method for free SO_2 described on page 112 of Food Analysis, International Chemical Series by A. G. Woodman, 4th Ed., McGraw-Hill Book Company, Inc., 1941, or Nichols and Reed: Ind. Eng. Chem., Anal. Ed., 1932. 79.

Results

LPCS Run No.	Free SO_2 ppm
65	199.34
	79.43
	123.6
	286.5
69	592.6
70	645
87	57

Discussion
Repeatable results were not obtained. This may have been due to the method of analysis. Using a 300 ppm SO_2 solution and the above analysis method, the results were 72.6 and 80 ppm. The SO_2 did not seem to react at a constant rate each time with the KI.

Another problem was freeze-drying a large enough sample to make repetitive analysis of the same batch.

APPENDIX IV

A. Drying Rate Data

Nomenclature

Run - Run number
Temp. - Temperature °F
Pressure - Pressure, mm Hg
Total Time - Total time that sample dried, min.
Weight In - Initial weight of sample, gms.
Weight Out - Final weight of sample, gms., as weighed
Measured Loss - Weight loss, gms., as indicated by drying rate apparatus
Time - Minutes since starting carrier flow
Wt. Loss - Loss in weight, gms., indicated by apparatus
Evaporation by Wt. - Per cent loss in weight by weighing sample
Evaporation Apparent - Per cent weight loss as indicated by apparatus and initial weight
Rate - Per cent wt. loss/minute, based on least-squares slope of initial constant rate.
Confidence Limits - 95% confidence limits on rate, %/minute
Intercept - Intercept of least-squares line with 0 time axis
C Slope - Per cent weight loss over which drying rate was assumed constant

B. Original data for this project (CE 9966) is contained in FMC Lab. notebooks (CEL-PDD) #160, 193, 220, 204, 188, and 171.

DRYING RATE DATA

RUN	82
TEMP	150
PRESSURE	6
TOTAL TIME	205
WEIGHT IN	7.10
WEIGHT OUT	1.95
MEASURED LOSS	5.05

TIME	WT LOSS
5.00	0.20
7.00	0.30
10.00	0.60
20.00	0.90
24.00	1.15
30.00	1.35
35.00	1.60
40.00	1.75
46.00	2.00
50.00	2.10
61.00	2.40
73.00	2.71
80.00	3.00
88.00	3.20

EVAPORATION BY WT	73.
EVAPORATION APPARENT	71.
RATE	0.59
CONFIDENCE LIMITS	0.05
INTERCEPT	0.07
CSLOPE	30.

DRYING RATE DATA

RUN	83
TEMP	150
PRESSURE	6
TOTAL TIME	171
WEIGHT IN	7.21
WEIGHT OUT	2.17
MEASURED LOSS	4.70

TIME	WT LOSS
3.00	0.07
5.00	0.20
20.00	0.82
30.00	1.30
35.00	1.60
41.00	1.80
55.00	2.30
60.00	2.60
68.00	2.85
76.00	3.12
85.00	3.40
105.00	3.82
115.00	4.10
137.00	4.37
153.00	4.60
171.00	4.70

EVAPORATION BY WT	70.
EVAPORATION APPARENT	65.
RATE	0.61
CONFIDENCE LIMITS	0.05
INTERCEPT	-0.02
CSLOPE	32.

DRYING RATE DATA

RUN	84
TEMP	150
PRESSURE	1
TOTAL TIME	245
WEIGHT IN	6.85
WEIGHT OUT	1.90
MEASURED LOSS	4.85

TIME	WT LOSS
9.00	0.30
15.00	0.63
20.00	0.80
28.00	1.16
35.00	1.49
40.00	1.69
50.00	2.00
65.00	2.50
76.00	2.85
85.00	3.10
90.00	3.30
95.00	3.45
125.00	4.10
142.00	4.50
170.00	4.75
197.00	4.80
225.00	4.85
245.00	4.85

EVAPORATION BY WT	72.
EVAPORATION APPARENT	71.
RATE	0.55
CONFIDENCE LIMITS	0.04
INTERCEPT	0.07
CSLOPE	42.

DRYING RATE DATA

RUN	85
TEMP	150
PRESSURE	6
TOTAL TIME	215
WEIGHT IN	6.72
WEIGHT OUT	1.82
MEASURED LOSS	5.25

TIME	WT LOSS
5.00	0.55
10.00	0.85
15.00	1.10
21.00	1.45
25.00	1.75
35.00	2.20
51.00	3.00
60.00	3.45
73.00	3.90
80.00	4.20
85.00	4.32
90.00	4.60
95.00	4.70
100.00	4.82
105.00	4.90
110.00	5.00
130.00	5.20
175.00	5.25
215.00	5.25

EVAPORATION BY WT	73.
EVAPORATION APPARENT	78.
RATE	0.78
CONFIDENCE LIMITS	0.04
INTERCEPT	0.34
CSLOPE	51.

DRYING RATE DATA

RUN	88
TEMP	150
PRESSURE	6
TOTAL TIME	190
WEIGHT IN	6.90
WEIGHT OUT	1.85
MEASURED LOSS	5.05

TIME	WT LOSS
5.00	0.20
15.00	0.50
20.00	0.80
25.00	1.00
30.00	1.20
35.00	1.45
40.00	1.70
45.00	1.80
50.00	2.05
61.00	2.52
70.00	2.82
80.00	3.10
90.00	3.42
100.00	3.60
110.00	3.86
120.00	4.00
130.00	4.10
140.00	4.20
150.00	4.35
160.00	4.55
175.00	4.65
190.00	5.05
210.00	5.30

EVAPORATION BY WT	73.
EVAPORATION APPARENT	73.
RATE	0.61
CONFIDENCE LIMITS	0.03
INTERCEPT	-0.05
CSLOPE	37.

DRYING RATE DATA

RUN	89
TEMP	150
PRESSURE	6
TOTAL TIME	275
WEIGHT IN	7.17
WEIGHT OUT	1.63
MEASURED LOSS	5.45

TIME	WT LOSS
5.00	0.27
10.00	0.40
15.00	0.55
20.00	0.80
25.00	0.95
30.00	1.10
35.00	1.22
40.00	1.40
45.00	1.45
50.00	1.60
55.00	1.75
65.00	2.00
75.00	2.20
85.00	2.40
97.00	2.71
112.00	3.00
147.00	3.80
165.00	4.00
175.00	4.30
180.00	4.42
195.00	4.70
215.00	5.05
236.00	5.25
245.00	5.45
260.00	5.60

EVAPORATION BY WT	77.
EVAPORATION APPARENT	76.
RATE	0.41
CONFIDENCE LIMITS	0.03
INTERCEPT	0.17
CSLOPE	28.

DRYING RATE DATA

RUN	90
TEMP	150
PRESSURE	6
TOTAL TIME	192
WEIGHT IN	7.14
WEIGHT OUT	1.67
MEASURED LOSS	5.70

TIME	WT LOSS
5.00	0.30
10.00	0.60
15.00	0.75
20.00	1.07
25.00	1.40
30.00	1.65
35.00	1.95
40.00	2.10
45.00	2.45
50.00	2.55
60.00	3.05
70.00	3.45
80.00	3.90
90.00	4.30
100.00	4.75
110.00	4.85
120.00	5.10
130.00	5.30
140.00	5.50
150.00	5.60
160.00	5.67
180.00	5.70

EVAPORATION BY WT	77.
EVAPORATION APPARENT	80.
RATE	0.71
CONFIDENCE LIMITS	0.04
INTERCEPT	0.08
SLOPE	43.

DRYING RATE DATA

RUN	91
TEMP	150
PRESSURE	6
TOTAL TIME	255
WEIGHT IN	7.13
WEIGHT OUT	1.47
MEASURED LOSS	5.80

TIME	WT LOSS
5.00	0.25
10.00	0.30
15.00	0.60
20.00	0.70
25.00	0.85
30.00	1.05
40.00	1.55
45.00	1.70
50.00	1.90
55.00	2.15
60.00	2.30
72.00	2.60
75.00	2.80
85.00	3.10
90.00	3.25
95.00	3.50
100.00	3.55
110.00	3.70
120.00	3.85
130.00	4.10
140.00	4.45
150.00	4.66
160.00	4.80
170.00	5.10
185.00	5.30
200.00	5.50
210.00	5.70
220.00	5.72
230.00	5.80
245.00	5.80
255.00	5.80

EVAPORATION BY WT	79.
EVAPORATION APPARENT	81.
RATE	0.53
CONFIDENCE LIMITS	0.03
INTERCEPT	-0.01
CSLOPE	36.

DRYING RATE DATA

RUN	93
TEMP	150
PRESSURE	6
TOTAL TIME	213
WEIGHT IN	7.06
WEIGHT OUT	1.64
MEASURED LOSS	5.60

TIME	WT LOSS
3.00	0.35
6.00	0.55
8.00	0.70
13.00	0.95
18.00	1.20
23.00	1.40
33.00	2.00
38.00	2.20
43.00	2.50
53.00	3.10
63.00	3.55
68.00	3.90
73.00	4.12
83.00	4.55
88.00	4.77
98.00	5.00
125.00	5.50
183.00	5.60
213.00	5.60

EVAPORATION BY WT	77.
EVAPORATION APPARENT	79.
RATE	0.76
CONFIDENCE LIMITS	0.03
INTERCEPT	0.23
CSLOPE	44.

DRYING RATE DATA

RUN	94
TEMP	150
PRESSURE	6
TOTAL TIME	195
WEIGHT IN	7.14
WEIGHT OUT	1.74
MEASURED LOSS	5.60

TIME	WT LOSS
5.00	0.25
10.00	0.58
22.00	1.35
25.00	1.55
30.00	1.80
35.00	2.30
50.00	2.95
70.00	3.85
80.00	4.20
85.00	4.25
90.00	4.50
95.00	4.65
105.00	5.10
115.00	5.25
125.00	5.32
135.00	5.50
145.00	5.55
155.00	5.55
165.00	5.60
195.00	5.60

EVAPORATION BY WT	76.
EVAPORATION APPARENT	78.
RATE	0.86
CONFIDENCE LIMITS	0.09
INTERCEPT	-0.01
CSLOPE	41.

DRYING RATE DATA

RUN	95
TEMP	150
PRESSURE	6
TØTAL TIME	185
WEIGHT IN	7.09
WEIGHT ØUT	1.58
MEASURED LØSS	5.60

TIME	WT LØSS
5.00	0.70
10.00	1.05
15.00	1.50
20.00	1.85
30.00	2.54
35.00	2.80
40.00	3.05
45.00	3.38
50.00	3.65
55.00	3.90
65.00	4.20
75.00	4.85
80.00	4.90
85.00	4.95
95.00	5.50
100.00	5.52
110.00	5.54
125.00	5.58
145.00	5.60
185.00	5.60

EVAPØRATIØN BY WT	78.
EVAPØRATIØN APPARENT	79.
RATE	1.10
CØNFIDENCE LIMITS	0.17
INTERCEPT	0.30
CSLØPE	26.

DRYING RATE DATA

RUN	96
TEMP	150
PRESSURE	6
TØTAL TIME	195
WEIGHT IN	7.06
WEIGHT ØUT	1.94
MEASURED LØSS	5.05

TIME	WT LØSS
5.00	0.55
10.00	0.78
20.00	1.15
25.00	1.32
30.00	1.65
35.00	1.90
40.00	2.20
45.00	2.40
50.00	2.60
55.00	2.85
60.00	2.95
65.00	3.10
70.00	3.30
75.00	3.40
80.00	3.55
85.00	3.80
90.00	3.95
95.00	4.10
100.00	4.10
110.00	4.50
120.00	4.62
135.00	4.90
160.00	5.05
185.00	5.05
195.00	5.05

EVAPØRATIØN BY WT	73.
EVAPØRATIØN APPARENT	72.
RATE	0.66
CØNFIDENCE LIMITS	0.05
INTERCEPT	0.27
CSLØPE	37.

DRYING RATE DATA

RUN	97
TEMP	150
PRESSURE	6
TOTAL TIME	155
WEIGHT IN	7.04
WEIGHT OUT	1.94
MEASURED LOSS	5.30

TIME	WT LOSS
5.00	0.45
10.00	0.95
20.00	1.60
25.00	1.85
30.00	2.15
35.00	2.50
45.00	3.10
55.00	3.70
65.00	4.15
80.00	4.70
97.00	5.05
115.00	5.30
125.00	5.30
135.00	5.30
145.00	5.30
155.00	5.30

EVAPORATION BY WT	72.
EVAPORATION APPARENT	75.
RATE	0.92
CONFIDENCE LIMITS	0.07
INTERCEPT	0.23
CSLOPE	44.

DRYING RATE DATA

RUN	100
TEMP	130
PRESSURE	4
TOTAL TIME	185
WEIGHT IN	7.19
WEIGHT OUT	0.66
MEASURED LOSS	6.55

TIME	WT LOSS
5.00	0.85
10.00	1.15
15.00	1.40
20.00	1.65
25.00	2.00
30.00	2.20
35.00	2.45
40.00	2.80
45.00	3.00
50.00	3.25
60.00	3.60
65.00	3.72
70.00	3.95
75.00	4.15
85.00	4.45
104.00	4.95
122.00	5.45
145.00	5.90
155.00	6.05
170.00	6.40
185.00	6.55
200.00	6.60
230.00	6.60

EVAPORATION BY WT	91.
EVAPORATION APPARENT	91.
RATE	0.74
CONFIDENCE LIMITS	0.03
INTERCEPT	0.60
CSLOPE	45.

DRYING RATE DATA

RUN	101
TEMP	130
PRESSURE	4
TOTAL TIME	195
WEIGHT IN	7.19
WEIGHT OUT	0.66
MEASURED LOSS	6.35

TIME	WT LOSS
5.00	0.30
10.00	0.58
15.00	0.90
20.00	1.30
25.00	1.55
30.00	1.95
40.00	2.35
45.00	2.65
50.00	3.05
55.00	3.35
60.00	3.60
70.00	4.00
75.00	4.20
80.00	4.47
90.00	4.70
95.00	4.90
105.00	5.20
110.00	5.40
120.00	5.60
125.00	5.80
130.00	5.95
135.00	6.10
140.00	6.25
145.00	6.25
150.00	6.35

EVAPORATION BY WT	91.
EVAPORATION APPARENT	88.
RATE	0.83
CONFIDENCE LIMITS	0.04
INTERCEPT	0.03
CSLOPE	50.

DRYING RATE DATA

RUN	102
TEMP	130
PRESSURE	4
TOTAL TIME	295
WEIGHT IN	6.54
WEIGHT OUT	0.96
MEASURED LOSS	5.80

TIME	WT LOSS
5.00	0.12
10.00	0.40
15.00	0.65
20.00	0.82
25.00	0.90
30.00	1.10
35.00	1.30
40.00	1.50
45.00	1.65
50.00	1.70
55.00	2.05
60.00	2.25
65.00	2.28
70.00	2.35
75.00	2.45
80.00	2.60
85.00	2.75
90.00	2.90
95.00	3.00
100.00	3.05
105.00	3.15
110.00	3.30
115.00	3.35
125.00	3.50
130.00	3.60
135.00	3.70
145.00	3.88
150.00	4.00
155.00	4.10
165.00	4.20
170.00	4.25
180.00	4.30
195.00	4.62
210.00	4.90
225.00	5.05
245.00	5.45
265.00	5.50
280.00	5.70
295.00	5.80

EVAPORATION BY WT	85.
EVAPORATION APPARENT	89.
RATE	0.56
CONFIDENCE LIMITS	0.05
INTERCEPT	0.02
CSLOPE	25.

DRYING RATE DATA

RUN	116
TEMP	150
PRESSURE	10
TOTAL TIME	115
WEIGHT IN	3.25
WEIGHT OUT	1.25
MEASURED LOSS	1.90

TIME	WT LOSS
2.00	0.25
5.00	0.35
10.00	0.55
15.00	0.80
20.00	0.95
25.00	1.18
35.00	1.48
40.00	1.65
45.00	1.75
55.00	1.86
65.00	1.90
90.00	1.90
115.00	1.90

EVAPORATION BY WT	62.
EVAPORATION APPARENT	58.
RATE	1.18
CONFIDENCE LIMITS	0.10
INTERCEPT	0.18
CSLOPE	46.

DRYING RATE DATA

RUN	117
TEMP	150
PRESSURE	10
TOTAL TIME	65
WEIGHT IN	3.30
WEIGHT OUT	1.21
MEASURED LOSS	1.86

TIME	WT LOSS
5.00	0.10
15.00	0.65
20.00	1.15
25.00	1.25
35.00	1.52
45.00	1.72
65.00	1.86

EVAPORATION BY WT	63.
EVAPORATION APPARENT	56.
RATE	1.84
CONFIDENCE LIMITS	1.02
INTERCEPT	-0.20
CSLOPE	38.

DRYING RATE DATA

RUN	118
TEMP	150
PRESSURE	10
TOTAL TIME	65
WEIGHT IN	3.15
WEIGHT OUT	1.18
MEASURED LOSS	1.62

TIME	WT LOSS
5.00	0.20
15.00	0.63
25.00	1.10
30.00	1.25
35.00	1.37
45.00	1.57
55.00	1.62
65.00	1.62

EVAPORATION BY WT	63.
EVAPORATION APPARENT	51.
RATE	1.36
CONFIDENCE LIMITS	0.23
INTERCEPT	-0.01
CSLOPE	40.

DRYING RATE DATA

RUN	119
TEMP	150
PRESSURE	19
TOTAL TIME	90
WEIGHT IN	3.15
WEIGHT OUT	1.25
MEASURED LOSS	1.85

TIME	WT LOSS
5.00	0.40
10.00	0.80
15.00	1.15
20.00	1.42
25.00	1.55
33.00	1.75
45.00	1.83
60.00	1.85
75.00	1.85
90.00	1.85

EVAPORATION BY WT	60.
EVAPORATION APPARENT	59.
RATE	2.17
CONFIDENCE LIMITS	0.56
INTERCEPT	0.09
CSLOPE	45.

DRYING RATE DATA

RUN	120
TEMP	150
PRESSURE	4
TØTAL TIME	100
WEIGHT IN	3.12
WEIGHT ØUT	1.22
MEASURED LØSS	1.50

TIME	WT LØSS
5.00	0.10
10.00	0.30
20.00	0.70
25.00	0.85
40.00	1.20
50.00	1.40
60.00	1.50
90.00	1.50
100.00	1.50

EVAPØRATIØN BY WT	61.
EVAPØRATIØN APPARENT	48.
RATE	1.22
CØNFIDENCE LIMITS	0.18
INTERCEPT	-0.08
CSLØPE	27.

DRYING RATE DATA

RUN	121
TEMP	150
PRESSURE	4
TOTAL TIME	60
WEIGHT IN	3.05
WEIGHT OUT	1.15
MEASURED LOSS	1.45

TIME	WT LOSS
5.00	0.10
10.00	0.40
15.00	0.55
20.00	0.80
25.00	1.05
30.00	1.20
40.00	1.40
60.00	1.45

EVAPORATION BY WT	62.
EVAPORATION APPARENT	48.
RATE	1.51
CONFIDENCE LIMITS	0.24
INTERCEPT	-0.11
CSLOPE	34.

DRYING RATE DATA

RUN	122
TEMP	150
PRESSURE	10
TØTAL TIME	55
WEIGHT IN	3.20
WEIGHT ØUT	1.32
MEASURED LØSS	1.70

TIME	WT LØSS
2.00	0.10
5.00	0.25
10.00	0.60
15.00	0.95
20.00	1.25
25.00	1.40
30.00	1.55
35.00	1.60
40.00	1.65
45.00	1.70
50.00	1.70
55.00	1.70

EVAPØRATIØN BY WT	59.
EVAPØRATIØN APPARENT	53.
RATE	2.04
CØNFIDENCE LIMITS	0.15
INTERCEPT	-0.05
CSLØPE	39.

DRYING RATE DATA

RUN	123
TEMP	150
PRESSURE	15
TOTAL TIME	75
WEIGHT IN	3.23
WEIGHT OUT	1.22
MEASURED LOSS	1.80

TIME	WT LOSS
5.00	0.15
10.00	0.45
15.00	0.80
20.00	1.05
30.00	1.40
35.00	1.55
40.00	1.70
45.00	1.75
55.00	1.80
75.00	1.80

EVAPORATION BY WT	62.
EVAPORATION APPARENT	56.
RATE	1.89
CONFIDENCE LIMITS	0.35
INTERCEPT	-0.15
CSLOPE	33.

DRYING RATE DATA

RUN	124
TEMP	150
PRESSURE	8
TOTAL TIME	80
WEIGHT IN	3.19
WEIGHT OUT	1.11
MEASURED LOSS	1.75

TIME	WT LOSS
5.00	0.15
10.00	0.40
15.00	0.70
20.00	0.90
25.00	1.15
30.00	1.32
35.00	1.42
45.00	1.65
60.00	1.75
80.00	1.75

EVAPORATION BY WT	65.
EVAPORATION APPARENT	55.
RATE	1.49
CONFIDENCE LIMITS	0.16
INTERCEPT	-0.06
CSLOPE	41.

DRYING RATE DATA

RUN	125
TEMP	150
PRESSURE	17
TOTAL TIME	75
WEIGHT IN	5.24
WEIGHT OUT	1.22
MEASURED LOSS	1.90

TIME	WT LOSS
5.00	0.40
10.00	0.80
15.00	1.15
20.00	1.30
25.00	1.40
43.00	1.80
50.00	1.90
75.00	1.90

EVAPORATION BY WT	62.
EVAPORATION APPARENT	59.
RATE	2.31
CONFIDENCE LIMITS	1.13
INTERCEPT	0.03
CSLOPE	35.

DRYING RATE DATA

RUN	127
TEMP	120
PRESSURE	4
TØTAL TIME	100
WEIGHT IN	3.19
WEIGHT ØUT	1.30
MEASURED LØSS	1.80

TIME	WT LØSS
5.00	0.05
10.00	0.35
15.00	0.55
20.00	0.85
25.00	1.05
35.00	1.20
40.00	1.50
60.00	1.65
75.00	1.65
90.00	1.80
100.00	1.80

EVAPØRATIØN BY WT	59.
EVAPØRATIØN APPARENT	56.
RATE	1.57
CØNFIDENCE LIMITS	0.20
INTERCEPT	-0.18
CSLØPE	33.

DRYING RATE DATA

RUN	126
TEMP	120
PRESSURE	10
TOTAL TIME	105
WEIGHT IN	3.22
WEIGHT OUT	1.30
MEASURED LOSS	1.90

TIME	WT LOSS
3.00	0.10
7.00	0.20
10.00	0.30
15.00	0.50
20.00	0.70
25.00	0.85
35.00	1.15
40.00	1.25
45.00	1.40
50.00	1.45
60.00	1.55
70.00	1.65
105.00	1.70

EVAPORATION BY WT	60.
EVAPORATION APPARENT	59.
RATE	1.06
CONFIDENCE LIMITS	0.08
INTERCEPT	-0.02
CSLOPE	36.

DRYING RATE DATA

RUN	129
TEMP	120
PRESSURE	19
TOTAL TIME	95
WEIGHT IN	3.20
WEIGHT OUT	1.18
MEASURED LOSS	2.00

TIME	WT LOSS
5.00	0.25
10.00	0.55
15.00	0.80
20.00	1.15
25.00	1.40
35.00	1.60
50.00	1.85
70.00	2.00
80.00	2.00
95.00	2.00

EVAPORATION BY WT	63.
EVAPORATION APPARENT	63.
RATE	1.81
CONFIDENCE LIMITS	0.16
INTERCEPT	-0.04
CSLOPE	44.

DRYING RATE DATA

RUN	130
TEMP	120
PRESSURE	10
TOTAL TIME	90
WEIGHT IN	3.19
WEIGHT OUT	1.16
MEASURED LOSS	1.83

TIME	WT LOSS
5.00	0.15
10.00	0.42
15.00	0.55
20.00	0.70
25.00	0.85
30.00	1.10
35.00	1.25
40.00	1.42
50.00	1.60
55.00	1.80
68.00	1.80
80.00	1.80
90.00	1.83

EVAPORATION BY WT	64.
EVAPORATION APPARENT	57.
RATE	1.11
CONFIDENCE LIMITS	0.09
INTERCEPT	0.01
CSLOPE	45.

DRYING RATE DATA

RUN	131
TEMP	120
PRESSURE	4
TOTAL TIME	110
WEIGHT IN	3.27
WEIGHT OUT	1.18
MEASURED LOSS	1.82

TIME	WT LOSS
5.00	0.15
10.00	0.50
15.00	0.65
20.00	0.85
25.00	1.00
30.00	1.10
35.00	1.25
40.00	1.45
50.00	1.50
55.00	1.55
75.00	1.65
80.00	1.75
90.00	1.80
95.00	1.82
100.00	1.82
105.00	1.82
110.00	1.82

EVAPORATION BY WT	64.
EVAPORATION APPARENT	56.
RATE	1.25
CONFIDENCE LIMITS	0.40
INTERCEPT	0.02
CSLOPE	31.

DRYING RATE DATA

RUN	132
TEMP	120
PRESSURE	6
TOTAL TIME	115
WEIGHT IN	3.22
WEIGHT OUT	1.22
MEASURED LOSS	1.75

TIME	WT LOSS
15.00	0.45
20.00	0.60
30.00	0.90
40.00	1.15
45.00	1.25
55.00	1.35
75.00	1.70
95.00	1.75
115.00	1.75

EVAPORATION BY WT	62.
EVAPORATION APPARENT	54.
RATE	0.84
CONFIDENCE LIMITS	0.10
INTERCEPT	0.06
CSLOPE	39.

DRYING RATE DATA

RUN	133
TEMP	120
PRESSURE	8
TOTAL TIME	70
WEIGHT IN	3.10
WEIGHT OUT	1.13
MEASURED LOSS	1.90

TIME	WT LOSS
10.00	0.45
25.00	1.05
35.00	1.30
45.00	1.55
55.00	1.65
65.00	1.75
70.00	1.90
90.00	1.90
100.00	1.90

EVAPORATION BY WT	64.
EVAPORATION APPARENT	61.
RATE	1.11
CONFIDENCE LIMITS	1.68
INTERCEPT	0.13
CSLOPE	42.

DRYING RATE DATA

RUN	134
TEMP	120
PRESSURE	15
TOTAL TIME	85
WEIGHT IN	3.19
WEIGHT OUT	1.21
MEASURED LOSS	2.00

TIME	WT LOSS
5.00	0.40
10.00	0.78
15.00	1.05
20.00	1.25
25.00	1.40
35.00	1.65
45.00	1.85
55.00	1.95
70.00	2.00
85.00	2.00

EVAPORATION BY WT	62.
EVAPORATION APPARENT	63.
RATE	2.04
CONFIDENCE LIMITS	2.53
INTERCEPT	0.09
SLOPE	33.

DRYING RATE DATA

RUN	136
TEMP	170
PRESSURE	4
TØTAL TIME	65
WEIGHT IN	3.13
WEIGHT ØUT	1.10
MEASURED LØSS	1.55

TIME	WT LØSS
5.00	0.10
10.00	0.60
15.00	0.80
25.00	1.15
35.00	1.35
45.00	1.45
50.00	1.50
55.00	1.55
60.00	1.55
65.00	1.55

EVAPØRATIØN BY WT	65.
EVAPØRATIØN APPARENT	50.
RATE	1.58
CØNFIDENCE LIMITS	1.35
INTERCEPT	-0.02
CSLØPE	37.

DRYING RATE DATA

RUN	137
TEMP	170
PRESSURE	15
TOTAL TIME	80
WEIGHT IN	3.10
WEIGHT OUT	1.2?
MEASURED LOSS	1.95

TIME	WT LOSS
5.00	0.40
10.00	0.85
15.00	1.25
25.00	1.60
30.00	1.70
50.00	1.95
70.00	1.95
80.00	1.95

EVAPORATION BY WT	61.
EVAPORATION APPARENT	63.
RATE	2.74
CONFIDENCE LIMITS	1.18
INTERCEPT	-0.02
CSLOPE	40.

DRYING RATE DATA

RUN	136
TEMP	170
PRESSURE	1
TOTAL TIME	95
WEIGHT IN	3.28
WEIGHT OUT	1.32
MEASURED LOSS	1.60

TIME	WT LOSS
5.00	0.30
10.00	0.55
15.00	0.75
20.00	1.00
25.00	1.15
30.00	1.40
40.00	1.45
60.00	1.50
95.00	1.60

EVAPORATION BY WT	60.
EVAPORATION APPARENT	49.
RATE	1.40
CONFIDENCE LIMITS	0.19
INTERCEPT	0.08
CSLOPE	30.

DRYING RATE DATA

RUN	139
TEMP	170
PRESSURE	6
TOTAL TIME	85
WEIGHT IN	3.31
WEIGHT OUT	1.29
MEASURED LOSS	1.95

TIME	WT LOSS
5.00	0.10
10.00	0.30
15.00	0.60
20.00	0.85
25.00	1.00
30.00	1.10
40.00	1.25
45.00	1.45
55.00	1.60
65.00	1.65
75.00	1.80
85.00	1.95

EVAPORATION BY WT	61.
EVAPORATION APPARENT	59.
RATE	1.54
CONFIDENCE LIMITS	0.34
INTERCEPT	-0.18
CSLOPE	26.

DRYING RATE DATA

RUN	140
TEMP	170
PRESSURE	19
TOTAL TIME	60
WEIGHT IN	3.20
WEIGHT OUT	1.16
MEASURED LOSS	1.75

TIME	WT LOSS
5.00	0.35
15.00	1.00
20.00	1.20
25.00	1.40
30.00	1.60
35.00	1.70
40.00	1.75
45.00	1.75
55.00	1.75
60.00	1.75

EVAPORATION BY WT	64.
EVAPORATION APPARENT	55.
RATE	1.65
CONFIDENCE LIMITS	0.66
INTERCEPT	0.13
CSLOPE	44.

DRYING RATE DATA

RUN	142
TEMP	150
PRESSURE	15
TOTAL TIME	105
WEIGHT IN	3.09
WEIGHT OUT	1.18
MEASURED LOSS	1.95

TIME	WT LOSS
10.00	0.48
12.00	0.62
15.00	0.75
20.00	1.00
22.00	1.10
25.00	1.20
27.00	1.30
30.00	1.33
35.00	1.50
40.00	1.60
45.00	1.67
55.00	1.85
65.00	1.95
85.00	1.95
105.00	1.95

EVAPORATION BY WT	62.
EVAPORATION APPARENT	63.
RATE	1.55
CONFIDENCE LIMITS	0.16
INTERCEPT	0.03
CSLOPE	39.

DRYING RATE DATA

RUN	143
TEMP	150
PRESSURE	50
TØTAL TIME	92
WEIGHT IN	3.10
WEIGHT ØUT	1.20
MEASURED LØSS	1.90

TIME	WT LØSS
2.00	0.25
4.00	0.45
7.00	0.55
12.00	0.80
17.00	1.15
22.00	1.25
27.00	1.45
32.00	1.55
37.00	1.60
42.00	1.70
47.00	1.80
52.00	1.85
67.00	1.90
82.00	1.90
92.00	1.90

EVAPØRATIØN BY WT	63.
EVAPØRATIØN APPARENT	61.
RATE	1.82
CØNFIDENCE LIMITS	0.40
INTERCEPT	0.17
CSLØPE	37.

DRYING RATE DATA

RUN	144
TEMP	150
PRESSURE	8
TOTAL TIME	80
WEIGHT IN	3.02
WEIGHT OUT	1.12
MEASURED LOSS	1.70

TIME	WT LOSS
9.00	0.25
10.00	0.32
12.00	0.42
14.00	0.50
16.00	0.60
19.00	0.75
23.00	1.00
27.00	1.05
33.00	1.25
38.00	1.40
46.00	1.52
51.00	1.60
56.00	1.65
63.00	1.70
72.00	1.70
80.00	1.70

EVAPORATION BY WT	63.
EVAPORATION APPARENT	56.
RATE	1.55
CONFIDENCE LIMITS	0.20
INTERCEPT	-0.15
CSLOPE	35.

DRYING RATE DATA

RUN	146
TEMP	150
PRESSURE	30
TOTAL TIME	115
WEIGHT IN	3.00
WEIGHT OUT	1.16
MEASURED LOSS	1.60

TIME	WT LOSS
5.00	0.25
6.00	0.30
8.00	0.42
11.00	0.50
14.00	0.66
16.00	0.85
20.00	0.98
23.00	1.05
26.00	1.15
35.00	1.35
38.00	1.40
45.00	1.50
49.00	1.55
53.00	1.60
57.00	1.65
62.00	1.68
74.00	1.68
81.00	1.68
115.00	1.68

EVAPORATION BY WT	61.
EVAPORATION APPARENT	56.
RATE	1.47
CONFIDENCE LIMITS	0.11
INTERCEPT	0.04
CSLOPE	38.

DRYING RATE DATA

RUN	147
TEMP	150
PRESSURE	20
TØTAL TIME	102
WEIGHT IN	3.20
WEIGHT ØUT	1.25
MEASURED LØSS	1.90

TIME	WT LØSS
3.00	0.25
8.00	0.50
10.00	0.60
14.00	0.75
18.00	0.95
23.00	1.15
29.00	1.35
33.00	1.45
37.00	1.50
44.00	1.65
49.00	1.70
53.00	1.80
61.00	1.85
82.00	1.90
93.00	1.90
98.00	1.90
102.00	1.90

EVAPØRATIØN BY WT	61.
EVAPØRATIØN APPARENT	59.
RATE	1.43
CØNFIDENCE LIMITS	0.14
INTERCEPT	0.12
CSLØPE	30.

DRYING RATE DATA

RUN	156
TEMP	150
PRESSURE	15
TØTAL TIME	101
WEIGHT IN	3.20
WEIGHT ØUT	1.24
MEASURED LØSS	1.75

TIME	WT LØSS
13.00	0.50
16.00	0.60
18.00	0.70
20.00	0.84
24.00	1.00
28.00	1.10
31.00	1.20
36.00	1.30
41.00	1.40
48.00	1.55
52.00	1.55
60.00	1.65
65.00	1.68
73.00	1.75
86.00	1.75
91.00	1.75
101.00	1.75

EVAPØRATIØN BY WT	61.
EVAPØRATIØN APPARENT	55.
RATE	1.13
CØNFIDENCE LIMITS	0.19
INTERCEPT	0.06
CSLØPE	41.

DRYING RATE DATA

RUN	157
TEMP	150
PRESSURE	10
TOTAL TIME	89
WEIGHT IN	2.90
WEIGHT OUT	1.08
MEASURED LOSS	1.80

TIME	WT LOSS
3.00	0.13
4.00	0.15
5.00	0.23
8.00	0.35
11.00	0.60
14.00	0.85
17.00	1.00
21.00	1.13
24.00	1.35
29.00	1.50
33.00	1.60
43.00	1.70
53.00	1.80
68.00	1.80
1.00	1.80
69.00	1.80

EVAPORATION BY WT	63.
EVAPORATION APPARENT	62.
RATE	2.08
CONFIDENCE LIMITS	0.26
INTERCEPT	-0.07
CSLOPE	39.

DRYING RATE DATA

RUN	158
TEMP	150
PRESSURE	5
TØTAL TIME	80
WEIGHT IN	3.04
WEIGHT ØUT	1.20
MEASURED LØSS	1.70

TIME	WT LØSS
5.00	0.12
7.00	0.23
10.00	0.45
12.00	0.60
15.00	0.75
17.00	0.90
20.00	1.00
23.00	1.05
28.00	1.15
35.00	1.35
40.00	1.40
45.00	1.50
50.00	1.60
55.00	1.65
60.00	1.70
65.00	1.70
70.00	1.70
80.00	1.70

EVAPØRATIØN BY WT	61.
EVAPØRATIØN APPARENT	56.
RATE	2.01
CØNFIDENCE LIMITS	0.22
INTERCEPT	-0.17
CSLØPE	33.

DRYING RATE DATA

RUN	159
TEMP	150
PRESSURE	15
TOTAL TIME	85
WEIGHT IN	3.17
WEIGHT OUT	1.09
MEASURED LOSS	1.92

TIME	WT LOSS
6.00	0.50
8.00	0.63
10.00	0.70
14.00	1.00
20.00	1.20
24.00	1.40
27.00	1.50
33.00	1.65
37.00	1.85
45.00	1.92
50.00	1.92
60.00	1.92
85.00	1.92

EVAPORATION BY WT	66.
EVAPORATION APPARENT	61.
RATE	1.56
CONFIDENCE LIMITS	0.25
INTERCEPT	0.23
CSLOPE	44.

DRYING RATE DATA

RUN	160
TEMP	150
PRESSURE	15
TØTAL TIME	105
WEIGHT IN	3.10
WEIGHT ØUT	1.00
MEASURED LØSS	1.92

TIME	WT LØSS
3.00	0.10
5.00	0.22
6.00	0.30
9.00	0.40
10.00	0.45
13.00	0.65
15.00	0.78
17.00	0.95
22.00	1.15
25.00	1.30
30.00	1.40
36.00	1.65
42.00	1.68
50.00	1.70
55.00	1.85
60.00	1.88
70.00	1.88
80.00	1.92
105.00	1.92

EVAPØRATIØN BY WT	66.
EVAPØRATIØN APPARENT	62.
RATE	1.79
CØNFIDENCE LIMITS	0.12
INTERCEPT	-0.06
CSLØPE	42.

DRYING RATE DATA

RUN	164
TEMP	120
PRESSURE	10
TOTAL TIME	75
WEIGHT IN	2.70
WEIGHT OUT	0.70
MEASURED LOSS	1.75

TIME	WT LOSS
2.00	0.02
5.00	0.20
7.00	0.32
10.00	0.50
14.00	0.62
16.00	0.85
20.00	0.92
25.00	1.20
31.00	1.30
45.00	1.45
55.00	1.70
75.00	1.75

EVAPORATION BY WT	74.
EVAPORATION APPARENT	65.
RATE	1.87
CONFIDENCE LIMITS	0.22
INTERCEPT	-0.04
CSLOPE	44.

DRYING RATE DATA

RUN	165
TEMP	120
PRESSURE	15
TØTAL TIME	90
WEIGHT IN	2.70
WEIGHT ØUT	0.80
MEASURED LØSS	1.55

TIME	WT LØSS
5.00	0.05
7.00	0.22
10.00	0.40
13.00	0.65
18.00	0.85
22.00	1.14
30.00	1.15
37.00	1.30
47.00	1.45
54.00	1.55
75.00	1.55
90.00	1.55

EVAPØRATIØN BY WT	70.
EVAPØRATIØN APPARENT	57.
RATE	2.30
CØNFIDENCE LIMITS	0.31
INTERCEPT	-0.22
CSLØPE	42.

DRYING RATE DATA

RUN	166
TEMP	120
PRESSURE	15
TOTAL TIME	85
WEIGHT IN	2.70
WEIGHT OUT	1.00
MEASURED LOSS	1.53

TIME	WT LOSS
3.00	0.07
5.00	0.20
7.00	0.30
10.00	0.45
13.00	0.58
17.00	0.95
20.00	1.00
25.00	1.15
28.00	1.30
32.00	1.32
42.00	1.46
45.00	1.50
55.00	1.50
58.00	1.53
75.00	1.53
85.00	1.53

EVAPORATION BY WT	63.
EVAPORATION APPARENT	57.
RATE	1.84
CONFIDENCE LIMITS	0.23
INTERCEPT	-0.04
CSLOPE	48.

APPENDIX V

DESIGN CONCEPT AND ESTIMATED COST OF FREEZE DRYING BY LPCS

This work was done by FMC Corporation for its own information and at its own expense. The objective was to assume an optimistic design and favorable operating conditions, based on the available data and from there to estimate the possible cost of freeze drying on a large scale by LPCS. The LPCS process flow sheet presents a concept which should work and which should represent a minimum cost.

The attached calculations give the essential information from which the cost of 4.7¢ per pound of water evaporated was calculated. This cost, to which must be added costs for frozen food storage, buildings, packaging, a site, and certain utilities is believed to represent some saving over an equivalent installation for vacuum freeze drying, but not enough to presently justify the restricted scope of possible foods and the complication of using the carrier vapor.

PROCESS CALCULATIONS

Basis 2,000 #/hr of water evaporated

Carrier flow heptane in at 130°F, out at 40°, with 20° of reheat in between

P in 10 mm Hg; out 4 mm Hg (total)

Food 80% moisture, 25 #/ft^3, particulate

PH_2O in approximately 0; PH_2O out approximately 1 mm Hg

Carrier Flow

To remove water at 3 moles heptane/mole H_2O evap.

To supply heat ΔH H_2O (solid 10° goes to vapor 40°) = 1233 BTU/#

ΔH heptane 130° - 40° + 20°, (.40 BTU/#°F) (130 - 40 + 20) °F = 44 BTU/#

Per # H_2O evaporated $\frac{1233}{44}$ = 28# heptane circulated

Or $\frac{28/100}{1/18}$ = 5.05 moles heptane/mole H_2O evap.

Therefore this much heptane will carry water away.

Total carrier flow 2,000 (28) = 56 10^3 #/hr

Bed Area and Volume; Contact

Bed area - for 2 passes at 137# heptane/ft^2 - hr for each pass
(Flow calculated to give pressure drop specified).

Area = $\frac{56\ 10^3\ \#/hr - pass}{137\ \#/hr - ft^2\ each\ pass}$ = 410 ft^2/pass or 820 ft^2 total.

Bed volume if cylindrical, 6" thick and area at average diameter = 820 ft^2

Volume = (820) (1/2) = 410 ft^3 total

Contact time, total:

$\frac{2{,}000\ \#\ H_2O/hr}{(.80\ \#\ H_2O/\#\ feed)\ (25\ \#/ft^3)}$ = 100 ft^3 feed/hr

Time = 4.1 hours total

Make bed a vertical cylinder, 20 ft high.

$$V = \frac{\pi}{4} (D_o - D_i)^2 h$$

$$D_o + D_i = 2 D_o - 1 = \frac{4V}{\pi h (D_o - D_i)} = \frac{4 (410)}{\pi 20 (1)} = 26.1 \text{ ft.}$$

Outside Diameter, $D_o = \frac{27.1}{2} = 13.6$ ft

Condenser Duty

Vapor at 40°F goes to liquid and solid at 0°F

ΔH H_2O = 1,238 BTU/# H_2O

ΔH heptane = 185 BTU/#

Q/# H_2O = 1,238 + 28 (185) = 6,357 BTU/# H_2O (use 6,500 BTU/#H_2O evap.)

Q total = 6,500 (2,000) = 13 10^6 BTU/hr = 1,080 tons of refrigeration

Condenser at 0°; refrigerant at -25°

Overall heat transfer coefficient for:

Vapor condensing outside
Calcium chloride solution film
Tube
Boiling liquid inside

U estimated at 100 BTU/hr ft^2 °F (Perry pg. 481)

Condenser Surface (stainless)

$$A = \frac{q}{U \Delta T} = \frac{13\ 10^6}{25 (100)} = 5.2\ 10^3 \text{ ft}^2$$

1" - 14 ga. tube, 20,000 ft.

Wt. = 27,000 #

LPCS COSTS - MAJOR EQUIPMENT

Condenser, 27,000 pounds (#) stainless steel (S. S.) at $2.00	$54,000
Brine HX, 6,800# S. S. at $2.00	13,600
Brine Evaporater, 2,500# S. S. at $2.00	5,000
Heptane Heater - Ammonia Cooler, 11,700# mild steel (M. S.) at $.75	8,800
Heptane Vaporizer, 5,500# M. S. at $.75	4,200
Drier - Heater, 3,300# M. S. at $.75	2,500
Basket, 11,600# S. S. at $2.00	23,200
Shield, 3,800 S. S. at $2.00	7,600
Rotating Drive	2,000
Shell, 70,000# M. S. at $.75	52,500
Lock Hoppers, 2 each 3,000# at $.75	4,600
Decanter, 6,000# at $2.00	12,000
LP Receiver, 6,000# at $.75	4,500
Rotary Valves, 10", 4 each at $3,000	12,000
Heptane Filter	1,000
Pumps, brine, heptane, ammonia, 3 each at $2,000	6,000
Elevator	15,000
Vacuum Pump	5,000
Boiler, 15,000#/hr + water treatment	25,000
Barometric Condenser	1,000
Total	259,500

LPCS CAPITAL COST SUMMARY

	Cost	Erection
Major Equipment	$259,500	2,500 Man Hours
Structure	30,000	600
Instruments and Controls	17,500	2,000
Piping and Valves	20,000	5,000
Platforms	6,000	300
Insulation	18,000	S/C
Electrical (explosion proof)	20,000	3,000
Foundations	5,000	1,000
Building, 1,000 ft^2 at 15,000	15,000	S/C
Paving and Drainage, Site preparation	8,000	S/C
Painting	3,000	1,000
Total Equipment	$402,000	15,400
Construction Labor at $3.50 plus 50% burden	$ 81,000	
Construction Supplies, Equipment	25,000	
Engineering (at 15% equipment)	72,500	
Procurement	15,000	
Refrigeration estimated by Lewis Refrigeration Co. for 1,080 Tons	600,000	
Total Capital Cost	$1,195,500	

Not Included

Electrical Sub Station
Site
Frozen Food Storage
Packaging
Product Storage
Carrier Purification Equipment

LPCS UNIT COST

Basis, 2,000# H_2O evaporation/hr
7,200 hours operation/year

Fixed Charges, (.20) 1.2 $(10)^6/7.2\ 10^3$	$33.33/hr
Power, 2,200 KW at $.012	26.40
Steam, 13,500#/hr at $1.00/1,000#	13.50
Labor, 2 men at $5.00	10.00
Overhead, 100% labor	10.00
Total	$93.23/hr

Or $\frac{93.23}{2,000} = 4.66$ ¢/# of H_2O evaporation

LPCS OPERATING COSTS

Estimated by Lewis Refrigeration Co., 2,200 KW total load.

Labor, 2 men at $5.00/hr

Overhead, 100% of labor

Steam, Evaporator, 2,300#/hr
Heptane Vaporizer, 10,600 #/hr
Radiant Heater
$q = 56\ 10^3\ (.43)\ 20 = 483{,}000$ BTU/hr
Steam = 483,000/924 = 520#/hr
Use 600#/hr

Total, 13,500#/hr at $1.00/1,000#

Fixed Charges,		
	Interest	6%
	Depreciation	10
	Maintenance	2
	Taxes and Insurance	2
	Total	20%/year

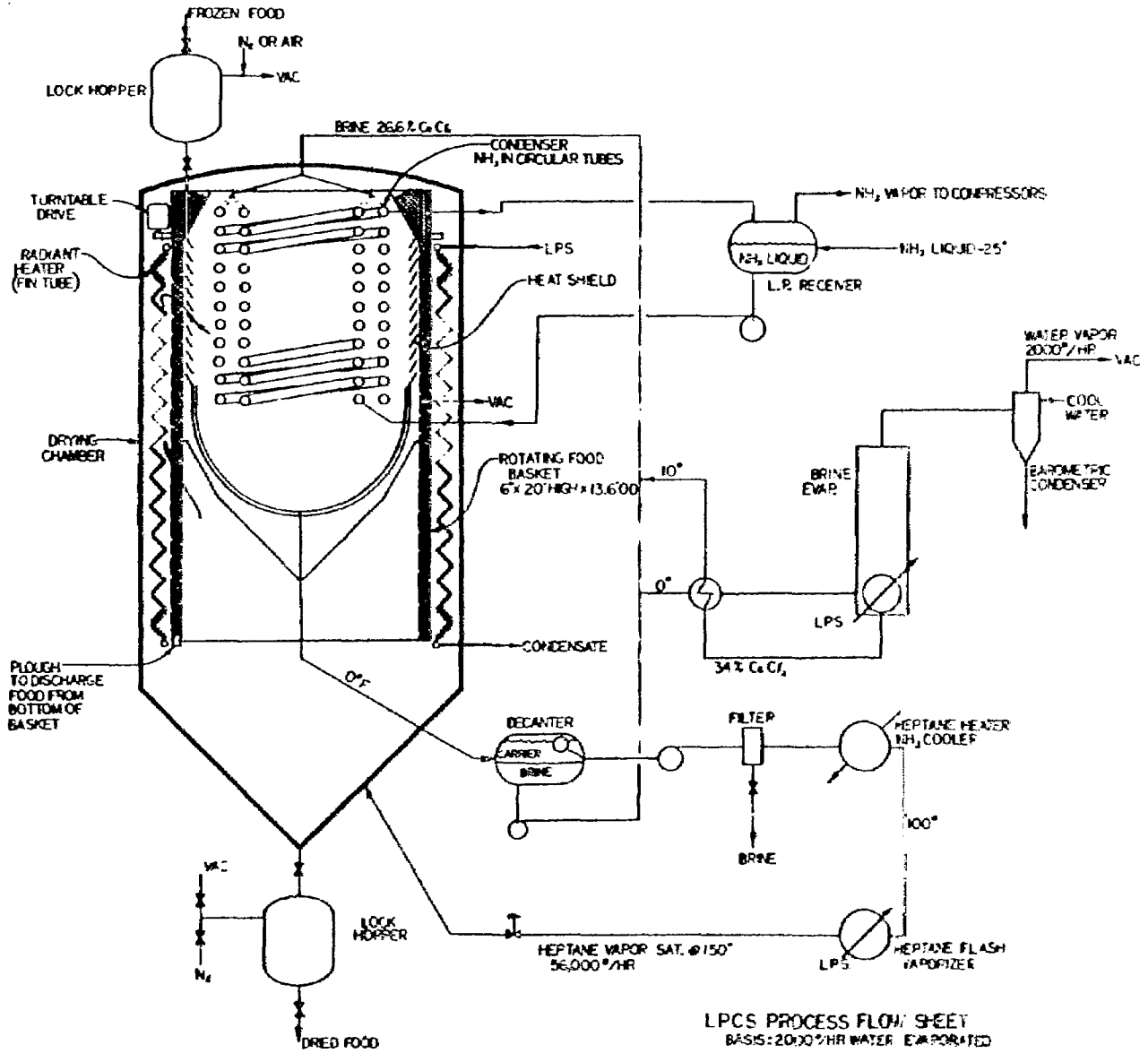


FIGURE V-1 APPENDIX LPCS PROCESS FLOW SHEET — BASIS: 2000 #/HR WATER EVAPORATED

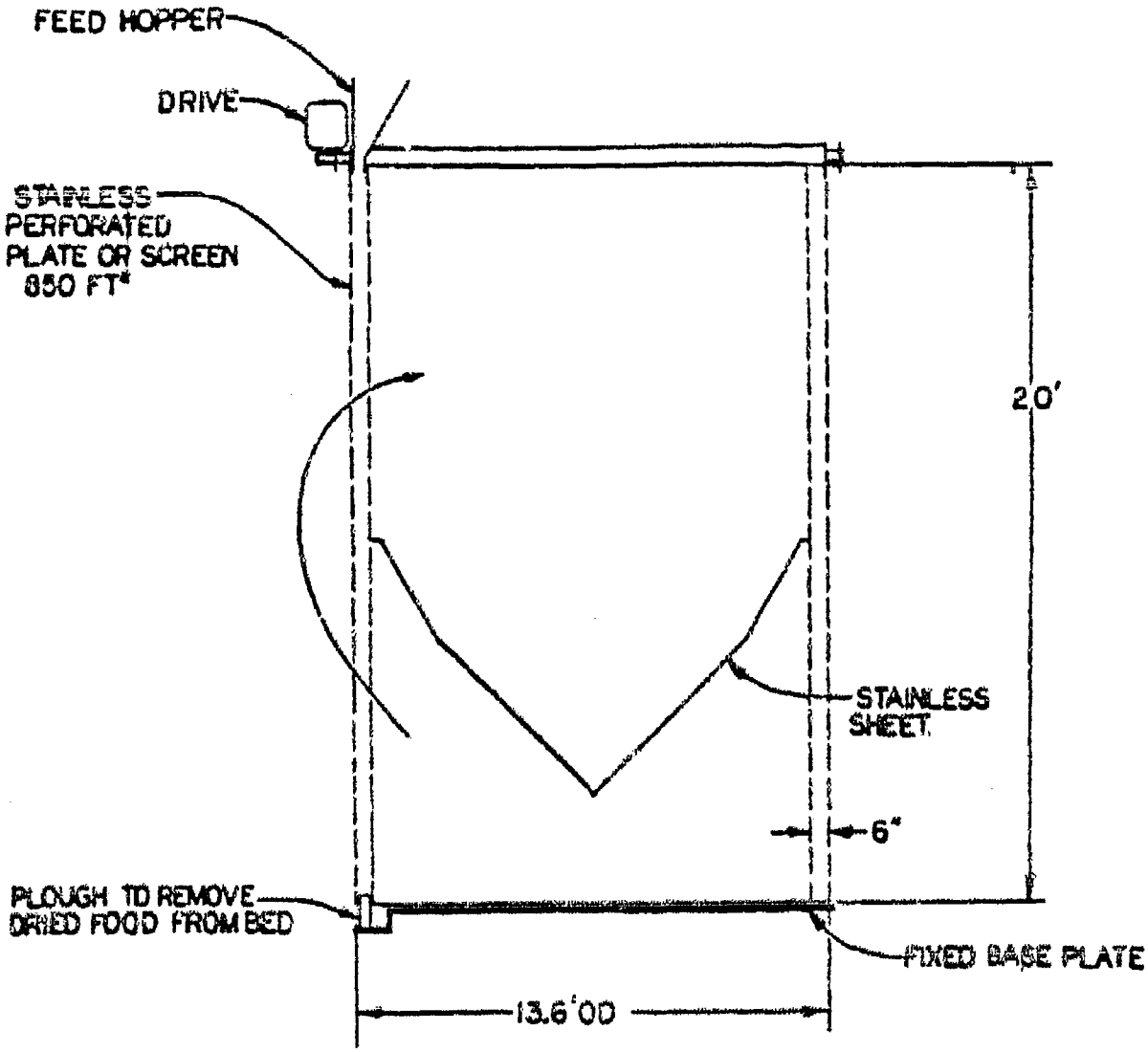


FIGURE V-2 APPENDIX DRYING BASKET- ROTATING

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1 ORIGINATING ACTIVITY (Corporate author) Central Engineering Laboratories FMC CORPORATION Santa Clara, California	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 REPORT TITLE

STUDY OF CARRIER GAS FREEZE-DRYING AT LOW PRESSURES

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (Last name, first name, initial)

Blaka, J. H.

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO. OF REFS
November 1965	150	14

8a CONTRACT OR GRANT NO. DA19-129-AMC-369(N) b PROJECT NO. 1K643303D548 c d	9a ORIGINATOR'S REPORT NUMBER(S) 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) FD-30

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	Process Development Branch, Food Division, U.S. Army Natick Laboratories, Natick, Mass

13 ABSTRACT

This report covers an investigation of a process to freeze-dry at increased rates by using condensible carrier vapors to transfer heat to frozen food particles (LPCS process). About 20 common foods were successfully dried. Optimum pressures are 3 to 15 mm Hg @ 130-150°F. A mixture of heptane isomers purified with fuming sulfuric acid appears to be the best carrier fluid for large-scale work, but formation of a solid hydrate in the condenser is a complication. Drying times ranged from 2 to 6 hours, and can be affected greatly by processing conditions.

DD FORM 1 JAN 64 1473

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Freeze-drying	8		7		9	
Foods	1,2		7		9	
Heat transfer	10		6		10	
Vapors	10		6		10	
Condensible	0		0		0	
Carrier	10		6		10	
Low pressure	5		6			
Low-pressure research					8	

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